A. F. State Library
JUL 17 1924

ABSTRACTS
OF
CHEMICAL PAPERS
ISSUED BY THE
BUREAU OF CHEMICAL ABSTRACTS

JUNE, 1924

BUREAU:

Chairman:
J. C. PHILIP, O.B.E., D.Sc., F.R.S.

Nominated by the Chemical Society:
J. I. O. MASSON, M.B.E., D.Sc.
G. T. MORGAN, O.B.E., D.Sc., F.R.S.
J. F. THORPE, C.B.E., D.Sc., F.R.S.
W. P. WYNNE, D.Sc., F.R.S.

Nominated by the Society of Chemical Industry:
E. F. ARMSTRONG, D.Sc., F.R.S.
J. L. BAKER.
E. V. EVANS, O.B.E.
Sir W. J. POPE, K.B.E., F.R.S.

A. PURE CHEMISTRY

Editor:
T. F. BURTON, B.Sc.

Assistant Editors:
H. M. DAWSON, D.Sc., B.Sc., Ph.D.
A. A. ELDRIDGE, B.Sc.
W. E. GARNER, M.Sc.
H. J. PAGE, M.B.E., B.Sc., A.I.C.
E. H. RODD, D.Sc.
E. E. TURNER, M.A., D.Sc.
H. WREN, M.A., D.Sc., Ph.D.

Adviser on Nomenclature:
A. J. GREENAWAY.

Indexer:
MARGARET LE PLA, B.Sc.

OFFICES OF THE BUREAU:
CENTRAL HOUSE, 46, FINSBURY SQUARE, LONDON, E.C. 2

Organic Chemistry.

Primary Products of the Combustion of Carbon. K. KULLGREN (*Gas- u. Wasserfach*, 1924, **67**, 226—229).—Carbon dioxide was the main product formed when air, freed from carbon dioxide, was passed over heated retort coke, at 260—410°, but 20% of its weight of carbon monoxide was always present. Dry air reduced the velocity, but did not affect the course of the oxidation. [Cf. *B.*, 1924, 457.] T. S. W.

Sulphochromic Oxidation of Organic Substances and Coals in Presence of Catalysts. D. FLORENTIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 228—230).—The oxidation of the carbon in organic compounds and coals to carbon dioxide by means of the sulphochromic mixture is complete in the presence of a small quantity of a mercury salt. With other catalysts (copper sulphate, silver chromate), or with no catalyst, a certain amount of carbon monoxide is produced also. E. E. T.

Preparation of *n*-Hexane. M. FAILLEBIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 160—161).—Pure *n*-hexane is prepared by the action of pulverised sodium on dry *n*-propyl bromide (Würtz reaction). The sodium is freed from sodium hydroxide by fusion under xylene and is then pulverised under the same liquid. E. E. T.

Conversion of [Solid] Paraffin by Heating under Pressure in the Presence of Hydrogen, Methane, and other Gases. H. I. WATERMAN and J. N. J. PERQUIN (*Proc. K. Akad. Wetensch.*, 1924, **27**, 132—139).—The results of further experiments are given. [Cf. *B.*, 1924, 500.] T. H. P.

Constitution of Melene. J. MARCUSSON and F. BÖTTGER (*Ber.*, 1924, **57**, [*B*], 633—635).—Melene, found by Pictet and Bouvier (A., 1915, i, 513) in coal, in vacuum-tar, in Galician paraffin, and in the products of distillation of beeswax, was assumed to be a solid naphthene, $C_{30}H_{60}$. The authors have now found that Indian paraffin, m. p. 59—60°, consists very largely of melene, which can be readily isolated by crystallisation from benzene and then from light petroleum. It has m. p. 62—63°, d^{65} 0·7913; d^{25} 0·9037; n^{90} 1·4228. Analyses indicate the composition $C_{30}H_{62}$; oxidation with strong hot nitric acid gave a mixture of aliphatic acids, whereas naphthenes under similar conditions gave nitro compounds. Similar differences in behaviour were found on oxidising catalytically with air in presence of manganese dioxide, melene yielding solid fatty acids, whilst naphthenes yielded polynaphthenic acids. Lastly, melene is slowly assimilated at 30° by *Bacterium aliphaticum*, which is incapable of attacking naphthenes. Melene is therefore a paraffin and not a naphthene. F. A. M.

Constitution of Kerogen. J. W. MCKINNEY (*J. Amer. Chem. Soc.*, 1924, **46**, 968—979).—A shale from Albert Mines, New Bruns-

wick, on extraction with acetone yielded 1·36% (calc. on the shale), which is about 4% of the kerogen. The hydrocarbons, amounting to 85% of the extract, on repeated fractionation in a vacuum yielded 15 separate fractions. These, by cooling, were split up into 28 different hydrocarbons consisting of the homologues: $C_{14}H_{30}$ to $C_{26}H_{54}$, $C_{12}H_{24}$ to $C_{24}H_{48}$, $C_{25}H_{48}$, d^{25} 0·8877, $C_{26}H_{50}$, d^{25} 0·8964. Of these, the two last do not appear to have been previously obtained. A. C.

Silver as Catalyst for the Absorption of Ethylene by Sulphuric Acid. W. Lommel and R. Engelhardt (*Ber.*, 1924, **57**, [*B*], 848).—The catalytic acceleration of the absorption of ethylene by sulphuric acid by means of silver salts (cf. Gluud and Schneider, this vol., i, 359) has been observed previously (cf. D.R.-P. 393632). The change consists in the successive addition of ethylene to the silver salt and production of ethyl hydrogen sulphate. Addition occurs very rapidly at the atmospheric temperature, whereas the second reaction does not take place with sufficient rapidity below 40°. The absorption of ethylene by aqueous solutions of silver nitrate (10%) and phosphoric acid (4%) may be used for the gas-analytical determination of ethylene; the gas can be removed subsequently by evacuating the solutions with a water-pump. H. W.

Formation of Metallic Acetylides. J. F. Durand (*Bull. Soc. chim.*, 1924, [iv], **35**, 161—171).—Acetylene is a very feeble acid (cf. A., 1902, i, 525) and the general methods of preparing salts are now applied to the formation of acetylides. By the action of pure acetylene on solutions of cupric hydroxide in concentrated potassium but not in sodium hydroxide, at 35° a reddish-brown precipitate, CuC_2, was obtained (cf. A., 1897, i, 309) which, immediately after preparation, yielded acetylene with hydrochloric acid or potassium cyanide, but after standing it polymerised and then gave with these reagents an organic, colloidal substance free from copper. Acetylene did not react with copper hydride, but with boiling solutions of zinc ethyl in light petroleum the white zinc acetylide, ZnC_2, was precipitated (A., 1923, i, 449), which gave pure acetylene with water and sodium hydroxide solution; it decomposed (without explosion) at 350° (cf. magnesium and alkaline-earth acetylides).

Solutions of acetylene in acetone gave with mercury ethyl a white, crystalline substance, the precipitation of which was reversible. Boiling solutions of mercury ethyl in light petroleum gave with acetylene gas mercury and carbon, the temperature being too high for carbide formation; boiling solutions of mercury and of lead phenyls in the same solvent gave no result, neither did a benzene solution of lead ethyl. Attempts to prepare aluminium acetylide, $Al_2(C_2)_3$, by the action of acetylene on aluminium carbide at 400—500° failed. E. E. T.

Preparation of Alkyl Chlorides. J. F. Norris and H. B. Taylor (*J. Amer. Chem. Soc.*, 1924, **46**, 753—757; cf. A., 1916, i, 461; 1920, i, 831).—Alcohols are converted into the corresponding

chlorides when heated for 1 hour under a reflux condenser with concentrated hydrochloric acid and zinc chloride. The lower alkyl halides may be purified from higher polymerides by heating gently under a reflux condenser with concentrated sulphuric acid. The best results are obtained when the molecular ratio of alcohol, hydrogen chloride (as concentrated hydrochloric acid), and zinc chloride is 1 : 2 : 2; yields varying from 60—82% were obtained. Alkyl chlorides were produced from the following alcohols: methyl, ethyl, *n*- and *iso*-propyl, *n*- and *sec*.-butyl, *iso*-amyl, pentan-β-ol, cetyl, β-phenylethyl, γ-phenylpropyl, *m*-nitrobenzyl, and *p*-nitrobenzyl. C. J. S.

Preparation of Various Aliphatic Halides and Halohydrin Compounds. M. T. Bogert and E. M. Slocum (*J. Amer. Chem. Soc.*, 1924, **46**, 763—768).—The method described by Adams and Vorhees (A., 1919, i, 306) for the preparation of alkyl iodides by the use of phosphorus and iodine has been modified so as to avoid the employment of special apparatus. Iodides have been obtained from *n*- and *iso*-propyl, *n*- and *iso*-butyl, and *iso*amyl alcohols (molecular ratio of alcohol, phosphorus, and iodine, 3 : 1 : 3). The trihalides of phosphorus may be used instead of the pentahalides for the conversion of propylene glycol into trimethylene bromide or iodide. Trimethylene bromohydrin and iodohydrin were prepared by passing the dry halogen hydride into propylene glycol; by conducting the operation in the presence of anhydrous benzene, a yield of 90% of the bromohydrin was obtained. A 50% yield of propylene glycol monoacetate was obtained by the action of acetyl chloride on propylene glycol. β-Chloroethyl acetate was obtained in very good yield by the action of a large excess of acetyl chloride on ethylene chlorohydrin. This method was applied to the production of *γ-bromopropyl acetate*, b. p. 88—90°/22 mm., when a yield of 90% was obtained. The best method for the preparation of γ-chloropropyl acetate consists in heating a mixture of propylene glycol, acetyl chloride, and zinc chloride in a sealed vessel for 8 hours at 100°. β-Iodoethyl acetate was obtained in 70% yield from the corresponding chloro compound by the action of excess of potassium iodide in methyl-alcoholic solution; γ-iodopropyl acetate was prepared in 88% yield by passing dry hydrogen iodide into an equimolecular mixture of propylene glycol and glacial acetic acid cooled to 0°. The *methylene ether* of *trimethyl iodohydrin*, $CH_2[O(CH_2)_3I]_2$, b. p. 180—193°/12 mm., was obtained (yield 60%) when a mixture of equimolecular proportions of trimethylene iodohydrin and trioxymethylene was saturated with dry hydrogen chloride, a second molecular proportion of the iodohydrin added, and the reaction completed by warming; it yields formaldehyde and iodopropyl alcohol when boiled with 20% sulphuric acid. C. J. S.

Action of Hydrogen Chloride on Methyl Alcohol. S. R. Carter and J. A. V. Butler (*J. Chem. Soc.*, 1924, **125**, 963).—A solution of hydrogen chloride (400 g.) in methyl alcohol (1 litre) on standing at 18° for 4 days becomes saturated with methyl chloride

which is then steadily evolved. The activity of methyl alcohol is thus far greater than that of higher alcohols. F. G. M.

Toxic Properties of Methyl Alcohol. S. Bodforss (*Svensk Kem. Tidskr.*, 1923, **35**, 333—335; from *Chem. Zentr.*, 1924, i, 574—575).—Methyl alcohol is toxic even when pure, and may exert a toxic effect when applied externally. G. W. R.

Determination of Methyl Alcohol. W. M. Fischer and A. Schmidt.—(See ii, 427.)

Detection of Methyl Alcohol. A. Kling and A. Lassieur.—(See ii, 428.)

Unsaponifiable Constituents (Higher Alcohols) of Shark and Ray Liver Oils. III. Y. Toyama (*Chem. Umschau*, 1924, **31**, 61—67; cf. A., 1923, i, 979).—Batyl and selachyl alcohols were prepared from the livers of *Chimœra barbouri* (Garman) and *Narcacion tokionis* (Tanaka). The analyses given by these preparations agreed better with formulæ containing 21 carbon atoms than with the formulæ containing 20 carbon atoms previously assigned to these alcohols. The solid portion of the unsaponifiable matter of these oils contains another alcohol homologous with batyl alcohol which is named *chimyl alcohol* and probably has the formula $C_{19}H_{40}O_3$. This alcohol occurs in the liver oils of several sharks and *Chimœra* and also in many cases is present in greater quantity than batyl alcohol. No trace of the unsaturated alcohol corresponding to chimyl alcohol could be found in these oils. Selachyl acetate had b. p. 242—244°/5 mm., n_D^{20} 1·4550, d_4^{20} 0·9417, iodine value (Wijs) 64·5, saponification value 260·0, molecular refraction 122·8 (calc. 122·0). Selachyl alcohol prepared from the acetate had b. p. 236—239°/5 mm., n_D^{20} 1·4691, d_4^{20} 0·9180, iodine value (Wijs) 79·5, molecular refraction 103·9 (calc. 103·3). The transformation of selachyl alcohol into batyl alcohol on hydrogenation was confirmed. By oxidising selachyl acetate with potassium permanganate in acetic acid solution nonoic acid and an acid of the formula $C_{11}H_{21}O(OAc)_2{\cdot}CO_2H$ were obtained. The formula

$$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}C_{11}H_{21}O(OH)_2$$

is therefore indicated as representing selachyl alcohol. The principal product obtained on the dry distillation of selachyl acetate is either oleyl alcohol or nonodecyl alcohol. H. C. R.

Methyl Ethyl Sulphate as an Alkylating Agent. T. K. Thayer (*J. Amer. Chem. Soc.*, 1924, **46**, 1044—1046).—*Methyl ethyl sulphate*, b. p. 198—200°/742 mm., is prepared by adding ethyl chlorosulphonate (1·3 equivalents) to a suspension of sodium methoxide in dry ether. The yield was 19·7% of the theoretical. The alkylating powers of methyl sulphate and methyl ethyl sulphate were compared by alkylating solutions of phenol. Using methyl sulphate, the yield of anisole was 74·2% of the theoretical. With methyl ethyl sulphate, 56·7% of the phenol was converted into anisole and 13·4% into phenetole, which shows that the methyl group has the greater alkylating power. A. C.

Laboratory Preparation of Ethyl Sulphate. E. V. Lynn and H. A. Shoemaker (*J. Amer. Chem. Soc.*, 1924, **46**, 999—1001).—A mixture of alcohol (50 g.) and concentrated sulphuric acid (104·5 g.) is allowed to drop on to anhydrous sodium sulphate (90 g.) in a flask fitted with a condenser and arranged for vacuum distillation. The flask is kept at 155—165° (optimum temp.) by an oil-bath and the pressure maintained at 20—45 mm. The mixture enters through a capillary tube at about 120—150 drops per minute. The time of distillation for the above quantities is 1 to 1½ hours. The ethyl sulphate is separated from the alcohol in the distillate, washed with dilute sodium carbonate and then with cold water, and dried over anhydrous sodium sulphate. The product (32·6 g.) is almost pure and is neutral to litmus. A. C.

Action of Mixed Dialkyl Sulphates on Mixed Organomagnesium Compounds. L. Bert (*Compt. rend.*, 1924, **178**, 1182—1184).—Methyl, propyl, *iso*propyl, *n*-butyl, and *iso*amyl ethyl sulphates were prepared by the action of ethyl chlorosulphonate on the corresponding sodium alkoxide. Bushong's observations (A., 1903, i, 732) on the *iso*propyl and *iso*amyl compounds were confirmed and the following constants are given for the methyl compound: b. p. 85°/15 mm., $d^{16·5}$ 1·228, $n_D^{16·5}$ 1·399. *Ethyl propyl sulphate* is a colourless oil, b. p. 107—108°/18 mm., $d^{16·5}$ 1·140, $n_D^{16·5}$ 1·411; *ethyl* n-*butyl sulphate*, a colourless oil, b. p. 117—118°/20 mm., d^{18} 1·112, n_D^{18} 1·415. Magnesium phenyl bromide reacts with all the above substances, yielding toluene in the case of methyl ethyl sulphate and ethylbenzene with the other four. H. J. E.

Explosive Decomposition of Glyceryl Trinitrate. Audibert (*Compt. rend.*, 1924, **178**, 1167—1169).—The decomposition of glyceryl trinitrate on explosion takes place in two stages; the first (explosive reaction) is represented by the equation $C_3H_5O_9N_3 \rightarrow 2CO+CO_2+2·5H_2+1·5N_2O+1·75O_2+21$ cal., whilst the second (residual reaction) gives rise to the final system, $3CO_2+2·5H_2O+1·5N_2+0·25O_2$, with a further evolution of 319 cal. Neither reaction is instantaneous; completion of the second depends on the conditions of reaction. H. J. E.

Action of some Halohydrins on Normal Sodium Phosphate in Aqueous Solution and on some Glycerophosphates. O. Bailly and J. Gaumé (*Compt. rend.*, 1924, **178**, 1191—1193).—Similar results to those obtained with the chlorohydrin of glycerol and normal sodium phosphate (Bailly, A., 1916, i, 113) were observed in the cases of the bromohydrin and the iodohydrin, but the two stages of the reaction were more clearly differentiated. The authors have prepared the *normal glycerophosphates* of *sodium*, *potassium*, and *strontium* and the *acid glycerophosphates* of *barium*, *strontium*, and *calcium*. H. J. E.

Ease of Oxidation of Organic Substances at the Ordinary Temperature. M. Gompel, A. Mayer, and R. Wurmser (*Compt. rend.*, 1924, **178**, 1025—1027).—Solutions of formic, acetic, propionic, oxalic, succinic, citric, lactic, and pyruvic acids, glycine,

alanine, and dextrose when shaken with blood charcoal at 40° evolve carbon dioxide. The rate of evolution of the gas is considerably affected by the presence and concentration of hydrogen ions, especially in the case of the acids of greater dissociation constant. The authors point out the biological significance of their observations. H. J. E.

Mechanism of Oxidation Processes. VII. H. WIELAND (*Annalen*, 1924, **436**, 229—262).—**I.** [With A. WINGLER.]—**Catalytic Fission and Oxidation of Keto-acids.**—Under the influence of palladium black, vegetable charcoal, and animal tissue, dilute aqueous solutions of keto-acids are hydrolysed with loss of carbon dioxide (cf. A., 1915, i, 354, 1046; 1916, i, 772). In this way, oxalacetic acid yields pyruvic acid, pyruvic acid gives acetic acid, malic acid yields acetic acid, and α-keto-β-phenylpropionic acid gives phenylacetic acid, benzaldehyde, benzoic acid, and oxalic acid. The reaction takes place in an atmosphere of nitrogen, provided that a hydrogen acceptor such as methylene-blue or *p*-benzoquinone is present. Traces of acetaldehyde were detected in experiments with pyruvic acid and washed animal tissue. The mechanism of the action is discussed.

II. [With H. LÖRENSKIOLD.]—**Mode of Reaction of Hydrogen Peroxide. Critical Experiments on Thunberg's Theory of Carbon Dioxide Assimilation** (cf. A., 1923, i, 1271).—On distilling hydrogen peroxide with pure lead carbonate the authors could detect no formaldehyde in the distillate, and Thunberg's results are considered to be due to the presence of traces of acetate in his lead carbonate. Only the slightest traces of formaldehyde were formed when formic acid was distilled with hydrogen peroxide, and the observation of Wislicenus (A., 1918, i, 472) that formic acid is formed in the oxidation of bicarbonates with hydrogen peroxide has been verified under conditions precluding the possibility of formic acid being introduced from atmospheric sources.

The results obtained by Dakin (A., 1908, i, 74) and Neuberg (A., 1915, i, 214, 215) in the oxidation of organic acids with hydrogen peroxide have been confirmed, but it is shown that the presence of ferrous iron is not essential. Comparative experiments with acetic acid and glycollic acid showed that formaldehyde was formed very much more rapidly in the latter case, and the view is expressed (cf. A., 1901, i, 310) that glycollic acid is the first stage in the oxidation of acetic acid with hydrogen peroxide. [Cf. i, 612.]

Glyoxylic acid, on oxidation with the same reagent, yields carbon dioxide and formic acid (cf. A., 1904, i, 474). In the case of butyric, crotonic, and β-hydroxybutyric acids, in addition to the aldehyde, considerable quantities of acetone are formed. Cinnamic acid yields chiefly the aldehyde; the saturated acid yields the aldehyde and ketone in approximately equal amounts. Malic acid, like succinic acid, is oxidised to acetic acid.

III. [With H. RAU.]—**Decomposition of Dihydroxyethyl Peroxide with Alkali** (cf. A., 1923, i, 650).—The decomposition of dihydroxyethyl peroxide with sodium hydroxide in the presence

of silver below 0° follows the course: $OH{\cdot}CHMe{\cdot}O{\cdot}O{\cdot}CHMe{\cdot}OH \longrightarrow 2Me{\cdot}CO_2H+H_2$, to the extent of 40%, whereas at 15° only 30% of the peroxide decomposes in this way. The alternative decomposition: $OH{\cdot}CHMe{\cdot}O{\cdot}O{\cdot}CHMe{\cdot}OH \longrightarrow Me{\cdot}CO_2Na+CHO{\cdot}Me+2H_2O$, has therefore the greater temperature coefficient. [Cf. also A., 1920, i, 709.] R. B.

Purification of Acetic Acid. K. J. P. Orton and A. E. Bradfield (*J. Chem. Soc.*, 1924, **125**, 960—961).—Acetic acid is best purified by distillation with chromium trioxide (2 g. per 100 c.c. of acid); the first 5% is rejected. The main fraction (85—90%), if distilled through an 8-pear still-head, melts at 16·2—16·4°, and is free from impurities which react with bromine. F. G. M.

Identity of Phocenic and Valeric Acids. E. André (*Compt. rend.*, 1924, **178**, 1188—1191).—Synthetic and natural valeric acids were found to have boiling points almost identical with those of specimens of phocenic acid obtained from dolphin-head oil and from porpoise fat. Amides of all four specimens exhibited almost identical melting points, which were unchanged on mixing the substances in pairs. The statement that phocenic acid is a mixture of butyric and caproic acids (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th ed., i, 152) is thus regarded as incorrect. H. J. E.

αβ-Dihalogenated Amylacrylic Acids. C. Moureu and M. H. Schindler (*Bull. Soc. chim.*, 1924, [iv], **35**, 171—178).—*αβ-Dibromoamylacrylic acid* [*αβ-dibromo-Δ$^{\alpha}$-octenoic acid*], a colourless liquid which will not crystallise, b. p. 144° (3 mm.), d_4^{18} 1·6444, $n_D^{19·5}$ 1·5320, is prepared by direct addition of bromine in chloroform solution to amylpropiolic acid. The *potassium*, *silver*, and two unstable *lead* salts, $(C_5H_{11}{\cdot}CBr{:}CBrCO_2)_2Pb$ and $(C_5H_{11}{\cdot}CBr{:}CBrCO_2)_2Pb{\cdot}PbO$, are described. *αβ-Di-iodo-Δ$^{\alpha}$-octenoic acid*, white needles, m. p. 47·5—49·5°, decomp. 100°, is prepared by direct addition of iodine to amylpropiolic acid, excess halogen being removed by sulphur dioxide. The *potassium* and *lead* salts are described; neither is very stable in solution. A basic *lead* salt was also obtained. The dihalogenated amylacrylic acids are less stable than the corresponding halogenated acrylic and crotonic acids. Attempts to separate the acids into isomerides by fractional distillation of the dibromo acid, fractional crystallisation of the di-iodo acid, and fractional crystallisation and precipitation of the salts all failed. The dibromo acid may be a mixture of two isomerides, one being in excess, and the crystals of the di-iodo acid may be a pure form. E. E. T.

Action of Carbonyl Chloride on Metallic Derivatives of Monosubstituted Acetylenes. I. Action of Carbonyl Chloride on Sodium *tert.*-Butylacetylide. M. P. Ivitzky (*Bull. Soc. chim.*, 1924, [iv], **35**, 357—360).—The sodium derivative of *tert.*-butylacetylene reacts readily with carbonyl chloride in ethereal solution yielding *trimethyltetrolyl chloride* [*γγ-dimethyl-*

Δ^{α}-pentinoyl chloride], $CMe_3 \cdot C{:}C \cdot COCl$, b. p. 46·5—47·5°/16 mm., which, on hydrolysis, yields γγ-dimethyl-Δ^{α}-pentinenoic acid, b. p. 106—107°/10 mm., m. p. 48—49°. The acid chloride can also react with a second molecule of the acetylide, and the unsaturated ketone, *bis-γγ-dimethyl-Δ^{α}-butinenyl ketone*, $(CMe_3 \cdot C{:}C)_2CO$, colourless crystals, m. p. 66·5°, is obtained as a by-product in the reaction. If the carbonyl chloride is added at once to the sodium *tert.*-butylacetylide, a violent reaction takes place, and after decomposition of the product with water, *tri-γγ-dimethyl-Δ^{α}-butinenyl carbinol*, $(CMe_3 \cdot C{:}C)_3C \cdot OH$, colourless crystals, m. p. 102·5°, is obtained. By the action of sodium *tert.*-butylacetylide on acetone a substance, m. p. 102·5°, was obtained in almost quantitative yield.

R. B.

Bauer Oil, the Higher-boiling Residue from Molasses Fusel Oil. A Source of Capric [Decoic] Acid. C. S. Marvel and F. D. Hager (*J. Amer. Chem. Soc.*, 1924, **46**, 726—730).—A dark reddish-brown oil, b. p. 130—235°/35 mm., obtained as a residue during the distillation of molasses fusel oil, consisted of the ethyl esters of decoic, lauric, myristic, and palmitic acids, and a little unsaponifiable matter. This forms an additional source for the preparation of decoic acid, which occurs only in small quantities in the common fats. [Cf. *B.*, 1924, 438.] C. J. S.

Glycerides of Fats and Oils. XI. Glycerides of Palm Kernel Oil. A. Bömer and K. Schneider (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 61—89).—Five almost pure mixed glycerides were isolated from a sample of palm kernel oil by repeated fractional crystallisation from acetone, and were identified as decoylomyristo-olein, myristodilaurin, laurodimyristin, palmitodimyristin, and myristodipalmitin. The first two of these glycerides were present in considerable amount, the third only in small amount, and the last two in very small amount, comprising the most difficultly soluble glycerides in the oil. It is very unlikely that stearic acid is present in the glycerides of palm kernel oil, and hexoic acid was not present in the sample investigated. It is uncertain whether decoic acid was present or not. H. C. R.

Chemical Composition of Sesamé Oil. G. S. Jamieson and W. F. Baughman (*J. Amer. Chem. Soc.*, 1924, **46**, 775—778).—Sesamé oil having the characteristics d_{25}^{25} 0·9187, n^{20} 1·4731, acid value 1·4, iodine value (Hanus) 110·8, saponification value 189·3, unsaponifiable matter 1·73%, acetyl value 9·8, Reichert-Meissl value 0·11, Polenske value 0·15, was found to contain the glycerides of the following acids in the proportions indicated: oleic (48·1%), linolic (36·8%), palmitic (7·7%), stearic (4·6%), arachidic (0·4%), and lignoceric (0·04%). C. J. S.

Oils and Fats from the Seeds of Indian Forest Plants. VI. Oil from the Seeds of *Aleurites montana*, Wilson. R. M. Parker, M. G. Rau, W. A. Robertson, and J. L. Simonsen (*Indian Forest Records*, 1923, **10**, 11—22).—The oil had the following characters: d_{15}^{15} 0·9467, n_D^{15} 1·494, acid value 3·4, saponification

value 203, unsaponifiable matter 0·6%, iodine value 141·4, insoluble fatty acids 94% (solidifying point 54—54·5°). The principal fatty acid present in the oil was β-elæostearic acid (m. p. 73°). The α-isomeride was apparently completely absent. The β-elæostearic acid was brominated in chloroform solution and an unstable *dibromo* derivative (m. p. 95°) obtained. On bromination in acetic acid solution, a mixture of a solid and a liquid tetrabromo acid was obtained. The solid product, needles, m. p. 115°, was not identical with the tetrabromo acid from linolic acid. The liquid acids present in the oil were identified as oleic and linolic acids; linolenic acid was absent. H. C. R.

Oils and Fats from the Seeds of Indian Forest Plants. VII. Oil from the Seeds of *Salvia plebeia*, R. Br. M. G. Rau and J. L. Simonsen (*Indian Forest Records*, 1924, **10**, 23—26).—The ground seeds on extraction with cold benzene gave 11% of an oil having the following characters: d_{30}^{30} 0·934, n_D^{30} 1·4832, acid value 6·0, saponification value 195·0, unsaponifiable matter 0·02%, acetyl value nil, iodine value 131·1, Reichert Meissl value 1·3, solidification point of the insoluble fatty acids 10·5—11°. Stearic acid was the only saturated acid present. Linolenic acid, linolic acid, and oleic acid were identified in the oil. H. C. R.

Tung Oil. A. Eibner, O. Merz, and H. Munzert (*Chem. Umschau*, 1924, **31**, 69—82).—Tung oil contains 75% of glyceryl α-elæostearate, which changes under the influence of light into the solid geometrical isomeride, glyceryl β-elæostearate. Both the α- and the β-triglycerides increase in weight at about the same rate when exposed to the air in thin films. After standing for 10 months in a closed brown glass bottle, β-elæostearin became insoluble in acetone and no longer melted, but charred at about 265°. Both α- and β-elæostearic acids, m. p. 48° and 72°, respectively, were prepared from tung oil which had stood for some time, by extracting with ethyl alcohol and fractionally crystallising the extract from this solvent at about 0°. Another acid (m. p. 106·5°), giving the reaction of azelaic acid with ferric and mercuric chlorides, was obtained from the residue insoluble in cold alcohol, and is presumably a cleavage product obtained from elæostearic acid. The difference in the drying properties of α- and β-elæostearic acids was investigated by exposing thin layers of the acids to the air. After 8—10 days, the α-acid was transformed into a clear yellow syrup, whilst the β-acid remained unchanged for 14 days and was only transformed into a clear yellow, viscous syrup after 4 weeks' exposure. Only two of the three possible geometrical isomerides of elæostearic acid have been obtained. It is considered that the α-acid is probably the *cis-cis* form and the β-acid the *cis-trans* form. Bromination of both α- and β-acids yields the same tetrabromide (m. p. 114°). The transformation of the α into the β geometrical isomeride, on treatment with bromine, is considered to be a peculiarity confined to compounds containing two double linkings separated by two methylene groups, a constitution which explains the high reactivity of elæostearic

acid. Evidence is adduced in favour of the view that the conversion of the α- and the β-acid plays very little part in the mechanism of the drying of tung oil, which appears to be a colloidal phenomenon involving transformation from the sol to the gel form rather than a case of molecular polymerisation. H. C. R.

Hydrate of Bismuth Lactate. E. Moles and R. Portillo (*Anal. Fís. Quím.*, 1924, **22**, 133—143).—Bismuth lactate obtained by the action of lactic acid on bismuth hydroxide contains water of hydration corresponding to the formula $C_6H_9O_6Bi,7Aq$. In solution, it behaves as a non-electrolyte, as is shown by cryoscopic and conductivity determinations. The solution, on keeping, deposits the anhydrous salt which has a smaller solubility than the hydrated salt. The reaction appears to be autocatalytic.
G. W. R.

Sebacic Acid. E. Bœdtker (*J. Pharm. Chim.*, 1924, **29**, 313—319).—Ricinoleic acid, when distilled with an excess of sodium hydroxide, gives sebacic acid, octyl alcohol, methyl hexyl ketone, and a viscous, brown residue. From the latter have now been isolated stearic acid, m. p. 69·2°, an acid, m. p. 81—82°, which is either ricinic acid, $C_{18}H_{34}O_3$, or hydroxystearic acid, undecenoic acid, $C_{11}H_{20}O_2$ (formed by the pyrogenic decomposition of the ricinoleic acid), and finally an asphaltic resin. The maximum yield of sebacic acid (33 g. from 100 g. of ricinoleic acid) is obtained by heating sodium ricinoleate with one equivalent of sodium hydroxide. F. G. M.

Resolution of Racemic Malic Acid and the Preparation of *d*-Malic Acid. E. Darmois and J. Perin (*Bull. Soc. chim.*, 1924, [iv], **35**, 353; cf. A., 1923, i, 299).—The *d*-malic acid obtained from active chlorosuccinic acid by treatment with silver nitrate according to Walden's process is now shown to be partly racemised, about 25% of the product consisting of the *l*-acid. By the addition of ammonium molybdate, it is possible to isolate successively the lævo- and dextro-rotatory forms of the ammonium dimolybdomalate, $2MoO_3,C_4H_6O_5,2NH_3$, the lævo-form crystallising first. Racemic ammonium dimolybdomalate does not appear to exist at the experimental temperatures, 16—20°, the crystals obtained when the compound is prepared from *r*-malic acid consisting of the *d*- and *l*-dimolybdomalate in equal proportions. A satisfactory method of converting the dimolybdomalonates into the corresponding malic acids has not yet been found, the product obtained from ammonium *l*-dimolybdomalonate being *l*-malic acid and not the *d*-form as was expected. R. B.

Resolution of Inactive Malic Acid into Optically Active Forms. H. D. Dakin (*J. Biol. Chem.*, 1924, **59**, 7—12).—From a solution of cinchonine and inactive malic acid in molecular proportions in hot methyl alcohol or acetone, *cinchonine l-malate* separates in very good yield, and may be completely purified by recrystallisation from methyl alcohol, or from water; from the latter solvent it separates in clear, hard prisms, m. p. 197—198°,

$[\alpha]_D^{19}$ +146° (in water). The methyl alcohol or acetone filtrate from the lævo salt is concentrated and water added occasionally; the residue is allowed to crystallise from water, when *cinchonine d-malate* ($+2H_2O$) is obtained as fine rosettes of clear, silky, prismatic needles, m. p. (hydrated) 106°, (anhydrous) 125—135°, $[\alpha]_D^{18}$ +153° (in water). On decomposition of the cinchonine salts with ammonia, *d*-malic acid, m. p. 99—100°, $[\alpha]_D^{19}$ +2·33°, and *l*-malic acid, m. p. 99—100°, $[\alpha]_D^{18}$ −2·31°, were obtained.

W. O. K.

Phosphor-Emetic [Potassium Phosphoryl Tartrate]. I. H. Sternlieb (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 211—214; cf. Costeanu, following abstract).—Crystals of potassium phosphoryl tartrate, $CO_2K{\cdot}CH(O{\cdot}PO){\cdot}CH(OH){\cdot}CO_2H,0{\cdot}5H_2O$, are prepared by dissolving 2 parts of phosphorus trioxide and 3 parts of potassium hydrogen tartrate in 16 parts of water and, with constant stirring, heating to the boiling point. The sparingly soluble, small, white crystals, having $[\alpha]_D^{18°}$ +80·62°, which separate, lose the water of crystallisation at 110°, and at 200° form a hygroscopic anhydride, m. p. 242°.

S. K. T.

Emetics [Cæsium Antimonyl Tartrate].—N. D. Costeanu (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 215—218; cf. Sternlieb, preceding abstract).—Three methods are given for the preparation of the hitherto unknown *cæsium emetic* (*cæsium antimonyl tartrate*), $CO_2Cs{\cdot}CH(O{\cdot}SbO){\cdot}CH(OH){\cdot}CO_2H,0{\cdot}5H_2O$. (1) By the action of diantimonyl tartaric acid (prepared by dissolving freshly-precipitated antimony oxide in cold tartaric acid solution and precipitating with alcohol) on normal cæsium tartrate solution, partly precipitating with alcohol, warming the mixture and cooling again. (2) By the interaction of cæsium chloride and silver antimonyl tartrate. (3) By boiling a solution of cæsium hydrogen tartrate with antimony oxide.

Cæsium antimonyl tartrate forms transparent, orthorhombic prisms, *d* 2·27, $[\alpha]$ +79·21°, loses its water of crystallisation at 100°, and, at 200°, forms an anhydride. The aqueous solution dissolves iodine, any remaining undissolved assuming a golden colour; it yields precipitates with silver and lead nitrates, ferric chloride, and mineral acids.

S. K. T.

Action of Triphenylmethyl Chloride on Free Sulphydro Groups. E. Bilmann and N. V. Due (*Bull. Soc. chim.*, 1924, [iv], **35**, 384—390; cf. A., 1905, i, 625; 1906, i, 625; 1908, i, 142).—The action of triphenylmethyl chloride or bromide on xanthylacetic acid proceeds in accordance with the scheme:

$$OEt{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2H+CPh_3Br \longrightarrow CPh_3{\cdot}S{\cdot}CO{\cdot}S{\cdot}CH_2{\cdot}CO_2H+EtBr$$
$$\longrightarrow COS+CPh_3{\cdot}S{\cdot}CH_2{\cdot}CO_2H.$$

The following compounds have been obtained: *Triphenylmethylthiolacetic acid*, $CPh_3{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, brilliant pointed prisms, m. p. 162·5—163°, which is not decomposed by warm dilute sodium hydroxide, but on treatment with bromine yields dithiolacetic acid and triphenylmethyl bromide; *α-triphenylmethylthiolpropionic*

acid, microscopic white crystals, m. p. 151°; *β-triphenylmethylthiolpropionic acid*, white, microscopic crystals, m. p. 208—209°; *triphenylmethylthiolsuccinic acid*, fine octahedra, m. p. 186—187° (decomp.).

In a similar way, the action of triphenylmethyl chloride on free xanthic acid in benzene solution yields triphenylmethyl xanthate, $CPh_3 \cdot S \cdot CS \cdot OEt$, large, yellow crystals, m. p. 139°, in a 97% yield. Free thiolbenzoic acid in toluene solution gives triphenylmethyl thiobenzoate, $C_6H_5 \cdot CO \cdot S \cdot CPh_3$, m. p. 187·5—188°, in 85% yield (cf. A., 1901, i, 636; 1913, i, 1335) and thiocyanic acid in ethereal solution gives an 89% yield of triphenylmethyl thiocyanate, $NCS \cdot CPh_3$, m. p. 137·5%. R. B.

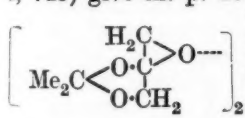
Alleged Reduction of Carbon Dioxide to Formaldehyde by Hydrogen Peroxide, and the Assimilation Hypothesis of T. Thunberg. A. Bach and M. Monosson (*Ber.*, 1924, **57**, [*B*], 735—738; cf. A., 1923, i, 1271).—The production of traces of formaldehyde on distilling basic lead carbonate with hydrogen peroxide was confirmed. The authors show, however, that the formaldehyde is not produced from the lead carbonate itself, but from the small amounts of organic preservatives (*e.g.*, acetanilide) used to stabilise the hydrogen peroxide, which are catalytically oxidised by the latter in presence of lead. Control experiments using purified materials gave completely negative results, whilst the addition of a little acetanilide led at once to the production of formaldehyde. The addition of barbituric acid, however, gave no trace of formaldehyde. Thunberg's assimilation hypothesis is therefore devoid of foundation. [Cf. i, 606.] F. A. M.

Electrolytic Oxidation of Formaldehyde. C. del Fresno (*Anal. Fís. Quím.*, 1924, **22**, 121—132; cf. Müller and Hochstetter, A., 1914, ii, 615; Müller, A., 1920, i, 709).—The author has studied the electrolytic oxidation of formaldehyde in solutions of sodium hydroxide with electrodes of platinum, copper, and silver, respectively. Curves are drawn showing the relation between anode potential and current intensity. The results are in agreement with the theories of Müller. In each case where the anode potential exceeds a certain value the current intensity decreases, and at the same time there is a discontinuity in the potential, which becomes more positive. The passage of a current begins at much lower potentials in alkaline solutions containing formaldehyde than in solutions of sodium hydroxide alone. With electrodes of copper and silver, oxidation of formaldehyde occurs accompanied by evolution of hydrogen (dehydroxidation) at low potentials, whilst at high potentials, as is the case also with platinum electrodes, oxidation occurs without evolution of hydrogen. The mechanism of the oxidation is discussed. G. W. R.

Production of Acetone by the Action of Potassium Acetate on Acetic Anhydride. E. Luce (*Bull. Soc. chim.*, 1924, [iv], **35**, 179—183).—The amount of acetone produced by refluxing acetic anhydride and potassium acetate for 30 hours at 170—180°

is not influenced by the presence of acetic acid. The yield of acetone is small, owing to polymerisation and to loss through carrying away by the carbon dioxide produced. The latter is prevented by special apparatus, and the yield then becomes 24% of the theoretical. No carbon monoxide is formed; sodium acetate cannot replace the potassium salt (cf. T., 1886, **49**, 317). Since the reaction is slow and at first no carbon dioxide is evolved, elevation of the temperature simply causing acetic anhydride to distil over; it probably follows the course $Ac_2O+Me\cdot CO_2K=(AcO)_2CMe\cdot OK=COMe_2+CO_2+Me\cdot CO_2K$. When potassium acetate is replaced by the butyrate, acetone and methyl propyl ketone are obtained. E. E. T.

Dihydroxyacetone. H. O. L. Fischer and H. Mildbrand (*Ber.*, 1924, **57**, [*B*], 707—710).—Dihydroxyacetone has been prepared in the unimolecular *form* [needles or rhombs, m. p. (indefinite) 65—71°] by the distillation of bimolecular dihydroxyacetone under greatly diminished pressure and immediate cooling of the distillate. It is converted by acetic anhydride and pyridine into the unimolecular diacetate, m. p. 42—45 [Dimroth and Schweizer (A., 1923, i, 745) give m. p. 46—47°]. With acetone in the presence of anhydrous copper sulphate, it yields the corresponding bimolecular *diisopropylidene ether*, needles, m. p. 165·5—167·5°, to which the annexed constitution is ascribed. Freshly distilled dihydroxyacetone is converted by ethyl orthoformate in alcoholic solution in the presence of ammonium chloride into the corresponding *ethylcycloacetal*, $\left[OH\cdot CH_2\cdot C(OEt)\cdot O\cdots CH_2\right]_2$, m. p. 126°. H. W.



Pennone [**ββγγ-Tetramethylpentane-δ-one**]. R. Locquin and W. Sung (*Compt. rend.*, 1924, **178**, 1179—1182; cf. A., 1923, i, 433, also Richard, A., 1911, i, 6).—In dehydrating ββγδ-tetramethylpentane-γδ-diol, only 6—7% of the substance is transformed into hexamethylacetone. The chief product (76%) is *ββγγ-tetramethylpentane-δ-one*, $C_9H_{18}O$, m. p. 63—64°, b. p. 167·5°/746 mm. (*oxime*, m. p. 125°, b. p. 215—220°; *semicarbazone*, m. p. 207—208°). On reduction by sodium and alcohol, the ketone, which the authors designate as *pennone*, yields the corresponding secondary alcohol, *pennol*, m. p. 50°, b. p. 179—180°. Oxidation of the ketone or alcohol yields *ααββ-tetramethylbutyric acid*, m. p. 200° (*ethyl* ester, a mobile liquid, b. p. 168—169°/746 mm.). H. J. E.

Reactions Relating to Carbohydrates and Polysaccharides. VIII. Electrolytic Reduction of Carbonyl Derivatives. H. Hibbert and R. R. Read (*J. Amer. Chem. Soc.*, 1924, **46**, 983—999).—Various ketones and aldehydes were reduced by an electrolytic method in order to compare the activities of the carbonyl group. The carbonyl derivative was added to an electrolyte (usually 2*N*-sulphuric acid with or without alcohol) in the cathode compartment, and caused a fall in the cathode potential varying with the ease or difficulty with which the substance underwent

reduction. In the case of aldehydes, this depended on (*a*), whether saturated or unsaturated: the fall was 0·12 volt for *n*-butaldehyde and 0·58 volt for crotonaldehyde; (*b*) the length of the chain; (*c*) the spatial relation of the atoms: the values for acetaldehyde, propionaldehyde, *iso*butaldehyde, and *n*-butaldehyde were 0·30, 0·30, 0·17, 0·12 volt, respectively; (*d*) character of groups in molecule: substitution of hydrogen by hydroxyl is shown by comparing *n*-butaldehyde 0·12 volt, with acetaldol, 0·25 volt. Ketones brought about a much smaller effect: dimethyl, methyl ethyl, and methyl propyl ketone showed 0·06, 0·06, and 0·04 volt, respectively. To compare the "current efficiencies," which were found to run parallel to the lowering of cathode potentials, the hydrogen absorbed was plotted against the total hydrogen as measured in a coulombmeter in series with the experimental cell. The reduction products of crotonaldehyde were found to be different from those obtained by chemical reduction. The main fraction consisted of 2 : 3-*dimethyl*-Δ^5-cyclo*pentene*-1-*aldehyde*: $\begin{matrix}CH_2\text{——}CH\\ |\quad\quad\ |\\ CHMe\cdot CHMe\end{matrix}\!\!>\!C\cdot CHO$, b. p. 170—175° (*semicarbazone*, white needles, m. p. 185—187°). Little or no dipropenyl glycol was formed. Dextrose could not be reduced to mannitol. The aldehydes investigated (apart from crotonaldehyde) were in all cases reduced to the corresponding alcohols, acetaldol to a glycol. The ketone reduction products were oily and had a pungent odour; they were not isolated. It is concluded that in the case of carbonyl derivatives such as the carbohydrates, anhydro-sugars, and polysaccharides, the determination of the two factors described results in values lying too close together to be of service as a means of distinguishing between the residual valencies of the carbonyl groups; and, further, that refinements in the measurements of the factors appear of little use owing to the limits imposed by the non-reproducibility of the cathode. A. C.

Course of the Mutarotation of Dextrose. H. v. Euler, K. Myrbäck, and E. Rudberg (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 28, 1—9).—According to Euler and Hedelius (A., 1920, i, 712), the reaction constant for this change is 6×10^{-3} in a solution having p_H 5 at 20°, and measurements made by Michaelis give the value $6{\cdot}6\times10^{-13}$ for the acid dissociation of dextrose at the same temperature. From these results, the concentration of the intermediate product or of the reacting ions is calculated to be $3{\cdot}7\times10^{-8}$. Since Michaelis employed dextrose solutions containing α- and β-dextroses in equilibrium in the known proportions, the authors have carried out experiments to ascertain if α-dextrose behaves, with respect to salt-formation, differently from β-dextrose or from the equilibrated mixture; no appreciable difference is found in this regard. Further, the degree of hydrolysis of the dextrose–alkali salt varies inconsiderably with the temperature. [Cf. Euler and Rudberg, A., 1923, ii, 840.] T. H. P.

Action of Guanidine on Dextrose in the Presence and Absence of Oxygen. E. J. Witzemann (*J. Amer. Chem. Soc.*, 1924, **46**, 790—794).—Morrell and Bellars (T., 1907, **91**, 1010) have shown

that guanidine is comparable with sodium and potassium hydroxides with regard to the velocity of hydrolysis of ethyl acetate. The results now described show that guanidine is also comparable with these bases in its action on dextrose both in the presence and absence of air or hydrogen peroxide. Guanidine causes polymerisation accompanied by yellowing more rapidly than potassium hydroxide, but this action is much less influenced by temperature than in the instance of the latter base. C. J. S.

Optical Behaviour of βε-Anhydroglucose, of βε-Anhydrogluconic Acid, and of βε-Anhydromannonic Acid. P. A. Levene (*J. Biol. Chem.*, 1924, **59**, 135—139).—Stereochemical considerations lead to the expectation that epichitose (βε-anhydroglucose) would not be able to form an oxide ring structure, and that it therefore exists in the aldehydic form. It is actually found that it is decolorised very rapidly by permanganate. Chitonic acid and chitaric acid do not exhibit mutarotation, probably because, likewise, lactone formation is not possible. W. O. K.

Preparation of α-Mannose. II. P. A. Levene (*J. Biol. Chem.*, 1924, **59**, 129—134).—A solution of mannose (100 g.) in water (25 c.c.) is cooled to 0°, and cooled glacial acetic acid (400 c.c.) is added. The crystals of α-mannose which separate are filtered after 4—5 hours, and subsequently extracted eight times with alcohol (80% by weight, 200 c.c., for each 100 g. of sugar). From optical observations on the mutarotation of α-mannose it is found that $K_1+K_2=0{\cdot}0054$, in 80% alcohol at 25°, and 0·0029 in water at 1·5°, where K_1 is the rate of conversion of the α- into the β-form, and K_2 the rate of the reverse reaction. From similar observations on β-mannose, $K_1+K_2=0{\cdot}0029$, in water at 1·5°, and 0·00575 in 80% alcohol at 25°. Measurements of solubility give $K_1=0{\cdot}00193$ and $K_2=0{\cdot}00041$. These results elucidate the discrepancy previously reported (Levene, this vol., i, 15). W. O. K.

α-Mannose Penta-acetate. P. A. Levene (*J. Biol. Chem.*, 1924, **59**, 141—144).—Acetylation of α-mannose in pyridine with acetic anhydride results in the formation of α-mannose penta-acetate, m. p. 64°, $[\alpha]_D^{17}$ +57·6°, identical with the penta-acetate obtained by Hudson and Dale (A., 1915, i, 502) by the action of zinc chloride on β-mannose penta-acetate. W. O. K.

Three Isomeric Crystalline Tetra-acetylmethyl-*d*-mannosides. J. K. Dale (*J. Amer. Chem. Soc.*, 1924, **46**, 1046—1051).—*α-Tetra-acetylmethyl*-d-*mannoside*, m. p. 65°, $[\alpha]_D^{20}$ +49·1°, was prepared by acetylating methyl-*d*-mannoside with acetic anhydride and sodium acetate. β-*d*-Mannose penta-acetate dissolved in glacial acetic acid saturated with hydrobromic acid yields a syrupy product containing bromine, which is converted by silver carbonate in the presence of methyl alcohol into *γ-tetra-acetylmethyl*-d-*mannoside*, m. p. 105°, $[\alpha]_D^{20}$ −26·6°. This compound possesses properties not generally characteristic of the acetylated glucosidic derivatives of the sugars. When subjected to alkaline hydrolysis, only three out of the four acetyl groups are removed,

although the whole four are removed by acid hydrolysis. On treating its solution in methyl alcohol with hydrogen chloride, a rapid change in rotation occurs and an apparent equilibrium is reached in a few minutes at $[\alpha]_D^{20}$ +10·4°. The solution at this stage was neutralised, and yielded a third isomeride, *β-tetra-acetyl-methyl*-d-*mannoside*, m. p. 162°, $[\alpha]_D^{20}$ −47·0°. Although the yield was only 7% of the theoretical, attempts to extract further crystalline substances were unsuccessful.

The close parallel in specific rotation and behaviour on hydrolysis between these isomerides and the three crystalline triacetylmethyl-*l*-rhamnosides recently prepared by Fischer, Bergmann, and Rahe (A., 1921, i, 94), is pointed out. A. C.

Isomeric Diacetonemannoses [Mannose Di*iso*propylidene Ethers]. P. A. Levene and G. M. Meyer (*J. Biol. Chem.*, 1924, **59**, 145—149).—Methylation of diacetonemannose by methyl iodide and silver oxide resulted in the formation of a *methyldiacetone-mannose*, b. p. 115°/1·2 mm., $[\alpha]_D^{20}$ +23° (in *s*-tetrachloroethane), which on hydrolysis by alcoholic hydrochloric acid yields mannose. Methylation by sodium and methyl iodide (cf. Freudenberg and Hixon, A., 1923, i, 1179) results in the formation of a methyldiacetonemannose, $[\alpha]_D^{20}$ −42·2° (in *s*-tetrachloroethane). These may be more or less pure samples of the α- and β-forms of α-methyl-βγεζ-diacetonemannoside, as from α-methylmannoside a diacetone-α-methylmannoside, b. p. 105°/0·5 mm., $[\alpha]_D^{20}$ +34·9°, was obtained. W. O. K.

Specific Rotations of Hexonic and α-Aminohexonic Acids and of their Salts. P. A. Levene (*J. Biol. Chem.*, 1924, **59**, 123—127).—The following specific rotations are given: gluconic acid, $[\alpha]_D^0$ 0·0°; mannonic acid, $[\alpha]_D^0$ +15·6°; gulonic acid, $[\alpha]_D^0$ +1·6°; galactonic acid, $[\alpha]_D^0$ −8·0°; allonic acid, $[\alpha]_D^0$ −10·0°; altronic acid, $[\alpha]_D^0$ +8·0°; whilst only sufficient idonic acid was available to ascertain that it is in all probability dextrorotatory. On comparison of these figures with those previously given for their sodium salts, phenylhydrazides, and amides, it appears that the rotation of the free acid is in the opposite sense from that of the derivatives. The following figures are also given: chitosaminic acid, $[\alpha]_D^0$ −1·3° in 5% sodium hydroxide solution (c = 5·0%), −15° in 2·5% hydrochloric acid; epichitosamic acid, $[\alpha]_D^0$ −5·0° in 5% sodium hydroxide solution (c = 5%), +10° in 2·5% hydrochloric acid solution; "dextro-*d*-xylos-α-aminohexonic acid," $[\alpha]_D^0$ −16° in 5% sodium hydroxide solution (c = 2·5%), +14° in 2·5% hydrochloric acid solution; "lævo-*d*-xylos-α-amino-hexonic acid," $[\alpha]_D^0$ +2·0° in 5% sodium hydroxide solution (c = 2·5%), −11° in 2·5% hydrochloric acid solution; chondrosaminic acid, $[\alpha]_D^0$ −15° in 5% sodium hydroxide solution (c = 2·5%), −17° in 2·5% hydrochloric acid solution; epichondrosaminic acid, $[\alpha]_D^0$ −1·8° in 5% sodium hydroxide solution (c = 2·5%), +8·0° in 2·5% hydrochloric acid solution, "dextro-*d*-ribos-α-aminohexonic acid," +2·0° in 5% sodium hydroxide solution (c = 2·5%), +12·5° in 2·5% hydrochloric acid solution; "lævo-*d*-ribos-α-amino-

hexonic acid," $-15°$ in 5% sodium hydroxide solution ($c = 2{\cdot}5\%$), $-26{\cdot}0°$ in 2·5% hydrochloric acid solution. W. O. K.

Relation between Rotatory Power and Structure in the Sugar Group. IV. Two Isomeric Crystalline Hexa-acetates of *d*-α-Mannoheptose. C. S. HUDSON and K. P. MONROE (*J. Amer. Chem. Soc.*, 1924, **46**, 979—983).—Acetylation of *d*-α-mannoheptose by adding the sugar to gently boiling acetic anhydride containing sodium acetate resulted in the isolation of a crystalline *hexa-acetate*, m. p. 106°, $[\alpha]_D^{20}$ $+24{\cdot}2°$ in chloroform. It was transformed by hot acetic anhydride and zinc chloride into a strongly dextrorotatory syrup from which a second *hexa-acetate*, m. p. 139—140°, $[\alpha]_D^{20}$ $-31°$ in chloroform, crystallised. From a comparison with the dextrose penta-acetate, it is inferred that the first hexa-acetate is a β-form and that the main (strongly dextrorotatory) amorphous product is the α-form. Comparison of the hexa-acetates with the galactose penta-acetates (A., 1916, i, 546) indicates that the compound, m. p. 106°, and the strongly dextrorotatory amorphous product are probably β- and α-forms of the butyleneoxide type, whereas the substance, m. p. 139—140°, is a β-form of some other type. A. C.

Polysaccharides. VIII. Molecular Structure of β-Hexa-amylose. J. C. IRVINE, H. PRINGSHEIM, and J. MACDONALD (*J. Chem. Soc.*, 1924, **125**, 942—947).—Karrer and Bürklin's statement (A., 1922, i, 435) that triamylose and β-hexa-amylose are identical is disproved by the conversion of the latter on exhaustive methylation into the crystalline β-*hexa(trimethylamylose)*, $C_{54}H_{96}O_{30}$, m. p. 102—105°, thus confirming the view of Pringsheim and Dernikos (A., 1922, i, 632). β-Hexa(trimethylamylose) on hydrolysis in methyl-alcoholic solution containing 1% of hydrogen chloride gave an equilibrium mixture of α- and β-trimethylmethylglucoside, which on further hydrolysis in 8% aqueous hydrochloric acid gave only 2 : 3 : 6-(βγζ-)trimethylglucose. F. G. M.

Synthesis of Amygdalic Acid from Gentiobiose. G. ZEMPLÉN (*Ber.*, 1924, **57**, [*B*], 698—704).—Gentiobiose octa-acetate is converted by successive treatment with methyl-alcoholic sodium methoxide solution, sodium hydroxide, and methyl sulphate, and finally with silver oxide and methyl iodide, into heptamethyl methylgentiobioside, long, colourless needles, m. p. 109°, $[\alpha]_D^{11}$ $-22{\cdot}39°$ in water, $[\alpha]_D^{16{\cdot}5}$ $-20{\cdot}89°$ in alcohol [Haworth and Wylam (T., 1923, **123**, 3124) give m. p. 106°, $[\alpha]_D$ $-33{\cdot}9°$ in water, $-29{\cdot}9°$ in alcohol]. On hydrolysis, it yields 2 : 3 : 5-trimethyl β-methylglucoside and 2 : 3 : 5-trimethylglucose. Gentiobiose octa-acetate is transformed by glacial acetic and hydrobromic acids in the presence of chloroform into acetobromogentiobiose,

$$C_{12}H_{14}O_3(OAc)_7{\cdot}Br,$$

m. p. 131—133·5°, $[\alpha]_D^{19}$ $+111{\cdot}8°$ in chloroform, which is converted by silver *dl*-mandelate into *hepta-acetylgentiobiosidyl mandelate*, $C_{12}H_{14}O_{11}Ac_7{\cdot}CO{\cdot}CH{\cdot}PhOH$, small, colourless needles, m. p. 209° (decomp.) after softening at 205°, $[\alpha]_D^{17{\cdot}5}$ $-9{\cdot}73°$ in chloro-

form, and hepta-acetylamygdalic acid, m. p. about 90°, $[\alpha]_D^{15}$ +6·25° or +10·55° in chloroform. In its main features, synthetic hepta-acetylamygdalic acid closely resembles the product derived from amygdalin, but an exact comparison is rendered difficult by the amorphous nature of both compounds. A wide discrepancy is observed only in the specific rotation, which is attributed to the incomplete racemisation of the mandelic complex in the conversion of amygdalin into hepta-acetylamygdalic acid and to a partial resolution of silver *dl*-mandelate into its active components during the preparation of the synthetic acid (cf. Karrer and co-workers, A., 1921, i, 260). H. W.

Starch Grains. L. Rosenthaler (*Schweiz. Apoth.-Ztg.*, 1923, **61**, 654—659; from *Chem. Zentr.*, 1924, i, 451—452).—Starch grains from different plants may in some cases be distinguished by their behaviour towards methylene-blue, naphthylene-blue, and neutral-red, respectively. Observations are also recorded on the behaviour of different kinds of starch grains towards peptising reagents, acids, and alkalis. Whilst the results are of value for analytical purposes, they are nevertheless in many cases influenced strongly by experimental conditions. G. W. R.

Iodo Compounds of Simple αβ-*cyclo*Acetals of the Type of Starch Iodide. M. Bergmann (*Ber.*, 1924, **57**, [*B*], 753—755).—A solution of acetolmethyl*cyclo*acetal, $\left(\mathrm{OMe{\cdot}CMe{<}\begin{matrix}CH_2\\ |\\ O\end{matrix}}\right)_2$, in methyl alcohol is converted by iodine and potassium iodide below 0° into the *compound* $C_8H_{16}O_4I_4,KI$, very unstable, bluish-black prisms, m. p. 50—52° when rapidly heated. The methyl-*cyclo*acetal of acetoin gives a similar, but even less stable, *compound*, dark, steel-blue prisms. The formation of starch iodide is attributed to the presence in starch of similar oxygen rings, which cause addition of iodine and potassium iodide owing to their pronounced residual affinity. The polyamyloses do not behave in this manner. H. W.

Polymerisation of the Cellulose Molecule. P. Bary (*Compt. rend.*, 1924, **178**, 1159—1161).—A theoretical paper in which the two different types of reaction undergone by cellulose involving (*a*) no depolymerisation and a colloidal resultant, or (*b*) depolymerisation with a resultant which is less colloidal in its nature than cellulose, are considered. Cellulose is represented, not as $(C_6H_{10}O_5)_m$, but as $(C_6H_{10}O_5)_m,H_2O$, where m is very large, and the suggestion is put forward that hydrolysis and depolymerisation are effected by hydration of one of the oxygen linkings in the unit structure of the molecule. H. J. E.

Cellulose in Coal. F. Schulz and J. Hamackova (*Bull. Soc. chim.*, 1924, **35**, [iv], 183—187).—Cellulose was extracted from various recent lignites by Schorger's method (*J. Ind. Eng. Chem.*, 1917, **9**, 556). The maximum content was 12% (referred to the weight of lignite less moisture and ash). The cellulose, a greyish-white mass in the crude state, was recognised by hydrolysis to a

hexose and by conversion to cellobiose octa-acetate. Analyses showed that only in exceptional cases does the cellulose of wood remain unaltered, on the conversion of the latter into coal, up to the tertiary geological age. Other coals and lignites yielded no trace of cellulose. E. E. T.

Effect of 5*N*-Nitric Acid on Cellulose, Dextrose, Natural and Artificial Humic Acids, and Lignin. H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 257—262; from *Chem. Zentr.*, 1924, i, 562).—The action of 5*N*-nitric acid on natural and artificially prepared humic acids and on lignin is similar, nitrophenolic substances occurring amongst the products of reaction. Cellulose and dextrose behave differently. Humic acid artificially prepared from sugar is more readily attacked than natural humic acid and lignin. G. W. R.

[Esterification and Mercerisation of Cellulose.] R. O. HERZOG and G. LONDBERG (*Ber.*, 1924, **57**, [*B*], 750; cf. this vol., i, 373).—The authors' inability to obtain a monoacetate or monobenzoate of cellulose is due to the fact that further esterification occurs more rapidly in the altered layers than does monoacylation in the deeper layers. H. W.

Acetylation of Lignin. E. HEUSER and W. ACKERMANN (*Cellulosechemie*, 1924, **5**, 13—21; 30–31).—Lignin was obtained by treating resin-free wood meal with 41·2% hydrochloric acid; the product contained 13% of methoxyl and was free from residues of pentosan. This was acetylated by heating with acetic anhydride in the presence of pyridine; the acetyl value increased up to a maximum corresponding with 32·5% of combined acetic acid and then decreased on further heating owing to hydrolysis of the ester. Acetylation with acetyl chloride gave substantially identical results. Acetic anhydride alone gave inferior acetylation values as compared with those obtained in the presence of pyridine; addition of sodium acetate was still less favourable to esterification. Much more rapid esterification was effected by a mixture of acetic anhydride and nitric acid, and the same maximum limit of acetyl value was attained. On further treatment, this acetyl value decreased as before, but subsequently increased up to 42·5% owing to hydrolysis and re-acetylation of groups originally combined as methoxyl. The acetyl-lignin esters obtained were lighter in colour than the original lignin. Natural lignin existing in wood probably contains three hydroxyl groups on Klason's formula; the triacetate, $C_{41}H_{37}O_{11}(OAc)_3$, should contain 20·07% of combined acetic acid, as against 17·8% calculated from the authors' equilibrium value duly corrected. J. F. B.

Humic Acids. I. Method of Preparation. H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 191—195; from *Chem. Zentr.*, 1924, i, 600).—Rosenthal coal used for the preparation of humic acids contained 3·7% of material extractable by benzene. The ethyl alcohol extract (18·9%) contained 55% of humic substances. The humic acid used in subsequent

investigations was obtained as follows. The coal was first extracted repeatedly with benzene and ethyl alcohol and the residue treated with 1% hydrochloric acid, after which it was shaken with 2*N*-sodium hydroxide. The alkaline solution was separated by filtration and centrifuging, and the humic acids were precipitated by acidifying with hydrochloric acid. The precipitate was collected and washed with water to the stage of incipient sol formation. The yield of humic acid was 60%, having the composition carbon 54·7%, hydrogen 3·0%, and ash 10·2%. G. W. R.

Humic Acids. II. Products of Alkali Fusion and Heating under Pressure. H. Tropsch and A. Schellenberg (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 196—213; from *Chem. Zentr.*, 1924, i, 600—601; cf. preceding abstract).—Humic acid (40 g.) obtained from bituminous coal was heated with potassium hydroxide (160 g.) and water (100 c.c.) at 240—300°. Humic substances were obtained in 40—50% yield. Steam distillation of the acid solution gave 3% of volatile acids, principally acetic acid together with a little formic acid, and small quantities of neutral reducing compounds. The ethereal extract contained *iso*phthalic acid, and hydroxy-*iso*phthalic acid or hydroxyterephthalic acid. Oxalic acid was obtained from the residue after ether extraction. Heating humic acid under pressure with 10*N*-potassium hydroxide for 140 hours at 150° yielded 52% of humic substances soluble in alkali, containing carbon 47·9%, hydrogen 2·6%, and ash 26·7%. From these products, after acidification, acetic acid and formic acid were isolated by steam distillation, and oxalic acid by extraction with ether. *m*-Hydroxybenzoic acid and 5-hydroxy*iso*phthalic acid were also obtained. G. W. R.

Humic Acids. III. Action of Nitric Acid on Humic Acids. H. Tropsch and A. Schellenberg (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 214—234; from *Chem. Zentr.*, 1924, i, 601—602; cf. preceding abstracts).—Humic acid from coal is rapidly attacked by 5*N*-nitric acid at 60°, and by prolonged heating the material goes into solution with the exception of 4—9% of solid, brown residue. Oxalic acid and certain strongly acid substances having the character of nitrophenols are obtained. Reduction of these nitro compounds gives black, humic substances. From the ethereal extract in certain cases, 5% (calculated on the original humic acid) of *trinitrodihydroxybenzene* is obtained. It forms yellow needles, m. p. 267° (decomp.). On drying in a vacuum, water of crystallisation is lost at 80°, and the composition is then given by the formula $C_6H_3O_8N_3,0{\cdot}5H_2O$. A crystalline *tin* double salt is obtained on reduction with tin and hydrochloric acid; it forms thick, well-formed crystals. On attempting to isolate the amino compound, decomposition takes place with formation of black, humic substances. The products of reaction of humic acid with nitric acid (*d* 1·4) or with 2·5*N*-nitric acid are similar. With nitric acid (*d* 1·5), however, nitrohumic acid is obtained. The action of 5*N*-nitric acid on humic acid prepared from quinol is more energetic than is the case with humic acid prepared from natural products. Oxalic

acid and substances of the character of nitrophenols are obtained. Humic acid from sugar gives, with 5*N*-nitric acid at room temperature, a red, amorphous substance similar to the nitrohumic acid obtained from natural humic acid by the action of nitric acid (*d* 1·5). With nitric acid (*d* 1·5), sugar humic acid yields 20% of substances of the character of nitrophenols. G. W. R.

Humic Acids. IV. Effect of certain Reagents on Humic Acids. H. Tropsch and A. Schellenberg (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 235—247; from *Chem. Zentr.*, 1924, i, 602; cf. preceding abstracts).—Humic acid from coal yields, with 72% sulphuric acid, 87·5% of humic substances, of which 22% is soluble in alcohol; 11·4% of volatile acids, including formic acid and acetic acid, and 1·8% of an orange-red, lacquer-like substance. Hydrochloric acid reacts in a similar manner. By chlorination of humic acid suspended in *s*-tetrachloroethane, substances containing 18 to 30·8% of chlorine are obtained. Among the products of reaction of potassium chlorate and hydrochloric acid on humic acid is hexachloroethane. G. W. R.

Humic Acids. V. Dry Distillation of Humic Acid and its Alkaline Derivatives. H. Tropsch and A. Schellenberg (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 248—256; from *Chem. Zentr.*, 1924, i, 603; cf. preceding abstracts).—Dry distillation of humic acid at 525° and 0·8—5·1 mm. yields 57·5% of carbonaceous residue and gaseous products, including steam, carbon dioxide, and acetic and formic acids. Tarry substances were not obtained in the distillate. Similar products were obtained by distillation at 300° under atmospheric pressure. The humic substance obtained by heating humic acid with 10*N*-potassium hydroxide at 150° under pressure yields similar products on distillation. The substance obtained by heating humic acid with potassium hydroxide at 300° behaves differently on distillation in that it yields a certain amount of tar both at atmospheric and under reduced pressures. From the products of distillation under reduced pressure, a wax-like substance having m. p. 62° is obtained, the composition of which corresponds with a ketone, $C_{47}H_{94}O$. Distillation of humic acid with zinc dust gives, in addition to gaseous products and an aqueous distillate, a certain amount of oil having b. p. 80—130°, which by the action of nitric acid yields a heavy oil having the odour of nitrobenzene. Among the products of the distillation of humic acid with zinc dust in a current of hydrogen is an oil having the odour of pyridine and quinoline. G. W. R.

Electrolytic Reduction of Acid Oximes. M. Ishibashi (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 335).—*γ-iso*Nitrosovaleric acid is so easily hydrolysed in acid solution that it cannot be reduced chemically to the corresponding amine. An 84% yield of the latter is, however, obtained by electrolytic reduction, employing a current density of 2 amp. per sq. dm., a temperature of 3—5°, and a sulphuric acid concentration of less than 5%. The amine from *α-iso*nitrosopropionic acid is obtained

in 95% yield with a current density of 4·5 amp. per sq. dm., a temperature of 7—10°, and an acid concentration of 8%.

W. T. K. B.

Trialdehyde Compounds of Primary Amines. M. Bergmann and A. Miekeley (*Ber.*, 1924, **57**, [*B*], 662—664; cf. Bergmann, Jacobsohn, and Schotte, this vol., i, 19).—Aliphatic aldehydes combine with primary amines to give trialdehyde compounds of the type $R\cdot CH<\begin{matrix}O\cdot CHR\\O\cdot CHR\end{matrix}>NR'$; the property is not shared by benzaldehyde.

Triformaldehyde-ethylamine, (R=H; R'=Et), b. p. 62—64°/42 mm. (*picrate*, m. p. 75°), is prepared by the gradual addition of ethylamine to a large excess of well-cooled, aqueous formaldehyde solution (30%). *Triacetaldehyde-ethylamine* is a colourless, unstable liquid, b. p. 59—60°/15 mm. Allylamine and formaldehyde give the relatively stable *triformaldehyde-allylamine*, b. p. 38—40°/1·5 mm., together with compounds richer in aldehyde. *Triacetaldehyde-allylamine* is a colourless, exceedingly unstable liquid, b. p. 48—50°/2·5 mm. Benzaldehyde and allylamine give *benzylidene-allylamine*, b. p. 96°/12 mm., which is transformed by bromine into *benzylidene-βγ-dibromopropylamine*, m. p. 36—37°. H. W.

Action of Secondary Amines on Alkyl Chlorosulphonates. M. Délépine and R. Demars (*Bull. Sci. Pharmacol.*, 1923, **30**, 577—599; from *Chem. Zentr.*, 1924, i, 415; cf. A., 1922, i, 634).—Dialkylaminosulphonic acids or their esters might be expected to be formed by the action of secondary amines on alkyl chlorosulphonates according to the equation:

$$2RR'NH+Cl\cdot SO_2\cdot OR''=RR'N\cdot SO_2\cdot OR''+NHRR',HCl.$$

Actually, however, compounds of the betaine type are obtained which may be considered as anhydrides of trialkylammonium hydroxide sulphonic acids. Their formation from dialkylaminosulphonic acids may be thus represented: $RR'N\cdot SO_2\cdot OR''\longrightarrow RR'R''N<\begin{matrix}SO_2\\O\end{matrix}\longleftarrow RR'R''N(OH)\cdot SO_2\cdot OH$. They are colourless neutral compounds which hydrolyse slowly with alkalis or acids to tertiary amines and sulphuric acid, behaving in this respect like the compounds formed from sulphur dioxide and tertiary amine oxides or hydroxylamines. *Trimethylammonium hydroxide N-sulphonic anhydride*, Me_3NSO_3, from dimethylamine and methyl chlorosulphonate, forms shining needles, m. p. above 200° (decomp.). It is also formed from sulphur dioxide and trimethylamine oxide. *Dimethylethylammonium hydroxide sulphonic anhydride*, Me_2EtNSO_3, has m. p. 131—133°, and *methyldipropylammonium hydroxide sulphonic anhydride*, m. p. 120—121°. G. W. R.

Constitution of Galegine. G. Tanret (*Bull. Soc. chim.*, 1924, [iv], **35**, 404—405; cf. A., 1914, i, 859).—One of the two open-chain structures advanced for galegine by Barger and White (this vol., i, 272) has been suggested previously by the author (Thesis, Paris, 1917). R. B.

Catalytic Decomposition of the Formic Amides. A. MAILHE (*Bull. Soc. chim.*, 1924, [iv], **35**, 363—365).—The primary amides of the formic acid series are dehydrated in contact with nickel at 400°, yielding the corresponding nitrile. The water formed in the reaction hydrolyses part of the unchanged amide to ammonia and the carboxylic acid, which in the presence of active nickel is decomposed into gaseous products and carbon. R. B.

Preparation of Diethylchloroaçetamide. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 209706).—Diethylchloroacetyl chloride, b. p. 93°/70 mm., obtained by chlorinating diethylacetyl chloride at about 100°, is shaken with excess of ammonia or of a compound evolving ammonia (*e.g.*, ammonium carbonate). The diethylchloroacetamide produced forms white flakes, m. p. 58°, and possesses valuable soporific properties. W. T. K. B.

The Oxime of Mesoxamide (Oximinomalonamide) and some Allied Compounds. V. Structural- and Stereoisomerism in the Methyl Ethers of the *p*-Tolyl Derivatives. A. PLOWMAN and M. A. WHITELEY (*J. Chem. Soc.*, 1924, **125**, 587—604; cf. *ibid.*, 1922, **121**, 2110).—Investigations of the ethers of alkyl- and aryl-substituted derivatives of oximinomalonamide have now been extended to the ethers of the *p*-tolyl derivatives, in which the stable yellow form appears to possess the *N*-ether structure. The yellow tautomeride of oximinomalon-*p*-toluidide, yellow scales, m. p. 170—171°, is obtained from mesox-*p*-toluidide and hydroxylamine under conditions (dilute alcoholic solution) which indicate that it possesses the *iso*oxime structure,

$$(C_7H_7\cdot NH\cdot CO)_2C<\overset{O}{\underset{NH}{|}}\!\!>,$$

whereas the colourless tautomeride, thin needles, becoming yellow at 150°, m. p. 170—171°, is formed under different conditions (absolute alcoholic solution) pointing to the oxime structure, $(C_7H_7\cdot NH\cdot CO)_2C{:}NOH$. Of the two *methyl ethers* of oximinomalon-*p*-toluidide, the colourless stable *isomeride*, m. p. 171° [*hydrate*, $(C_7H_7\cdot NH\cdot CO)_2C(OH)\cdot NH\cdot OH$, m. p. 196°] from its formation from the hydrated form of mesox-*p*-toluidide and α-methylhydroxylamine must be regarded as the *O*-ether, whilst the structure of the yellow *isomeride*, m. p. 182° (decomp.), is established as the *N*-methyl ether by its hydrolysis to β-methylhydroxylamine and mesox-*p*-toluidide, and by its synthesis from the same two compounds. Further work on oximinomalonmono-*p*-tolylamide has led to the isolation of three yellow and two colourless *isomerides*. The original yellow isomeride (α), m. p. 184°, is converted into a colourless isomeride (β), m. p. 157°, by spontaneous evaporation from alcohol, and into a second colourless isomeride (β′), m. p. 175°, by the action of moist hydrogen chloride in the presence of chloroform; each of these colourless isomerides yields a corresponding yellow tautomeride (γ and γ′) when crystallised from non-hydroxylic solvents, melting at the same temperature as the parent

colourless compound. On treatment with phosphorus pentachloride the β- and γ-isomerides yield p-*tolyloxamidonitrile*, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}CN$, colourless needles, m. p. 178°, together with carbon dioxide, a reaction which indicates that they are the two structural forms of *anti-p*-tolylmesoxamideoxime, the coloured γ-isomeride possessing the *iso*oxime structure, $\begin{matrix} C_7H_7{\cdot}NH{\cdot}CO \\ NH_2{\cdot}CO \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} NH \\ O \end{matrix}$. On treatment with phosphorus pentachloride the β′- and γ′-tautomerides undergo the normal Beckmann change and yield oxamide, carbon dioxide, and *p*-toluidine. They are therefore regarded as the structural isomerides of *syn-p*-tolylmesoxamideoxime, the true oxime structure, $NH_2{\cdot}CO{\cdot}C(:NOH){\cdot}CO{\cdot}NH{\cdot}C_7H_7$, being assigned to the colourless β′-isomeride. The α-isomeride is the most stable isomeride and forms the sole product of the action of nitrosyl chloride on malonmono-*p*-toluidide. It yields the same ethers as the β- and γ-forms, and is similarly decomposed by the action of phosphorus pentachloride; it probably possesses a nitrone structure,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(:NHO){\cdot}CO{\cdot}NH_2.$$

The action of methyl iodide on the α-, β-, and γ-isomerides in the presence of silver oxide yields an **O-*methyl ether***, colourless needles, m. p. 204°, a second colourless ***ether***, flat needles, m. p. 155°, being obtained from the β′- and γ′-isomerides under similar conditions. The structure of these isomeric ethers as the *anti-* and *syn*-forms, respectively, of oximinomalonmono-*p*-toluidide,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(:NOMe){\cdot}CO{\cdot}NH_2,$$

is deduced from the synthesis of the isomeride, m. p. 204°, by the condensation of α-methylhydroxylamine hydrochloride in aqueous alcoholic solution with *mesoxmono-*p*-toluidide*,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}CO{\cdot}NH_2,$$

m. p. 222° (decomp.), [*hydrate*, $C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)_2{\cdot}CO{\cdot}NH_2$, colourless plates, m. p. 222°, decomp., *phenylhydrazone hydrate*, colourless needles, yellow at 165°, m. p. 193°, *phenylhydrazone*, yellow needles, m. p. 193°], the hydrated form,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)(NH{\cdot}OMe)CO{\cdot}NH_2,$$

colourless needles, m. p. 179° (decomp.), being produced intermediately. Methylation with diazomethane converts the α-, β-, and γ-isomerides of oximinomalonmono-*p*-toluidide into an **N-*methyl ether***, bright yellow, felted needles, m. p. 200° (decomp.), the β′- and γ′-isomerides yielding a second yellow *isomeride*, m. p. 150°, decomp. (*hydrate*, colourless needles). The structure of these yellow isomerides as *N*-methyl ethers of the *anti-* and *syn*-forms, respectively, of oximinomalonmono-*p*-toluidide is indicated by their hydrolysis with moist hydrogen chloride to the hydrated form of the corresponding ketone, mesoxmono-*p*-toluidide, from which a small quantity of the yellow isomeride, m. p. 200°, is formed by the action of β-methylhydroxylamine, the main product of this latter reaction being a colourless additive compound,

$$C_7H_7{\cdot}NH{\cdot}CO{\cdot}C(OH)(N_2Me{\cdot}OH){\cdot}CO{\cdot}NH_2,$$

flat needles, m. p. 174° (decomp.), which has hitherto resisted dehydration.

Acetylation of the five isomerides of oximinomalonmono-*p*-toluid-

ide yielded one of two colourless *acetyl* derivatives, m. p. 132° and 165°, respectively. The former is obtained from the α-oximino compound, the latter from the β′- and γ′-isomerides, the β- and γ-isomerides yielding a mixture from which only the acetyl derivative, m. p. 165°, could be isolated. On hydrolysis the latter substance yields the β′-oximino compound, whilst the compound melting at 132° yields a mixture of the α- and β-isomerides. The acetyl derivatives are accordingly regarded as acetates of the *syn*- and *anti*-type, respectively. R. B.

Thermal Decomposition of Allophanic Esters. J. GRANDIÈRE (*Bull. Soc. chim.*, 1924, [iv], **35**, 187—196).—The following new esters were prepared by Béhal's method (A., 1919, ii, 301): *allophanates* of ethylpropylcarbinol (m. p. 185·5°); ethylbutylcarbinol (m. p. 187°), methyldiethylcarbinol (m. p. 152°), triethylcarbinol (m. p. 156°), methylethylpropylcarbinol (m. p. 148°), methylethylbutylcarbinol (m. p. 130°), Δ^{α}-penten-γ-ol (m. p. 155°), *o*-methyl*cyclo*hexanol (m. p. 177°), furyl alcohol (m. p. 167·5°), *o*-chlorophenol (m. p. 179°), glycol chlorohydrin (m. p. 182·5°).

On heating to 20° or 30° above the melting point most allophanic esters decompose into the alcohol and cyanuric acid, together with a small quantity of cyanic acid which reacts with the alcohol to give the corresponding urethane and allophanate. The esters of tertiary alcohols behave differently; a hydrocarbon of the ethylene series is evolved and allophanic acid probably formed as an intermediate product, but decomposes to carbamide, which immediately loses ammonia, both substances being unstable at the decomposition temperature of the ester. A certain amount of the alcohol and cyanuric acid is also formed.

The allophanates of geraniol, rhodanol, and citronellol decompose at 180—200° into carbon dioxide, ammonia, cyanuric acid, the alcohol, and a hydrocarbon, together with a brown, viscous liquid which, on hydrolysis, yields a small quantity of the corresponding alcohol. The allophanic esters of furyl and cinnamyl alcohols decompose into ammonia and carbon dioxide, leaving a resinous residue.

It is suggested that the behaviour of the allophanates of tertiary alcohols will serve for the detection of these alcohols (cf. A., 1919, ii, 301). E. E. T.

Isomeric Modifications of Methyleneaminoacetonitrile and their Biological Significance. T. B. JOHNSON and H. W. RINEHART (*J. Amer. Chem. Soc.*, 1924, **46**, 768—774).—Further investigation of the methyleneaminoacetonitriles, m. p. 129° and 86°, obtained by Klages (A., 1903, i, 469) has shown that they are structural isomerides having the formula $C_9H_{12}N_6$. The two compounds have different crystalline forms, behave differently on hydrolysis, and the one cannot be transformed into the other. The compound, m. p. 129°, for which the designation α-hydroformamine cyanide is proposed, forms orthorhombic crystals; β-hydroformamine cyanide, m. p. 86°, forms monoclinic crystals. C. J. S.

Deaminisation. III. Evidence of the Existence of Aliphatic Diazonium Salts from the Formation of Chloro-oximino Compounds. G. S. SKINNER (*J. Amer. Chem. Soc.*, 1924, **46**, 731—740).—The formation of ethyl chloro-oximinoacetate from the hydrochloride of ethyl aminoacetate and nitrous acid at low temperatures is presented as evidence of the existence of an aliphatic diazonium salt. It is believed to be produced according to the scheme: $NH_2 \cdot CH_2 \cdot CO_2Et, HCl \xrightarrow{+HNO_2} Cl \cdot N_2 \cdot CH_2 \cdot CO_2Et \xrightarrow{+HNO_2} Cl \cdot N_2 \cdot CH(N:O) \cdot CO_2Et \longrightarrow OH \cdot N:CCl \cdot CO_2Et$. A modifie dmethod is given for the preparation of ethyl and *n*-butyl diazoacetates. By the action of nitrous anhydride and of nitrosyl chloride on the ethyl diazoacetate a nitrile oxide, $C(:N:O) \cdot CO_2Et$, b. p. 132—133°/3 mm., d_4^{20} 1·2780, d_4^{25} 1·2726, was obtained which is unimolecular in benzene, bimolecular in ethylene dibromide, and intermediate in nitrobenzene; it has also been obtained from ethyl chloroaminoacetate and sodium carbonate. The decomposition of ethyl and *n*-butyl aminoacetates by nitrous acid in the presence of hydrochloric acid leads to the formation of the corresponding chloroacetates. Ethyl pyrazolinetricarboxylate, m. p. 98°, has been obtained by treating ethyl aminoacetate hydrochloride with nitrous acid in a manner described in the original and preserving the resulting liquid, b. p. 5—40°/4—5 mm., for several months. The preparation of *chloro-oximinoethane*, $CCl(:N \cdot OH) \cdot Me$, m. p. 84—85°, by the action of nitrous acid on ethylamine is described.

C. J. S.

Reactions of certain Aromatic and Aliphatic Derivatives. A. ANGELI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 109—116).—The author quotes fresh data confirming his rule concerning the analogy of behaviour exhibited between two groups united directly and the same groups occupying ortho- or para-positions in one and the same aromatic nucleus (cf. A., 1923, i, 1003).

With reference to the mobility which the alkoxy groups of an aromatic nucleus impress on the halogen atoms of side chains in the ortho- or para-position to such groups, Werner and Goldschmiedt have shown that, whilst the group $CHPhCl(\text{or Br}) \cdot$ resists the action of boiling alcohol, the analogous ortho- or para-substituted groups, $OMe \cdot C_6H_4 \cdot CHCl(\text{or Br}) \cdot$ and $CH_2O_2:C_6H_3 \cdot CHCl \cdot$, are readily converted into $OMe \cdot C_6H_4 \cdot CH(OEt) \cdot$ and $CH_2O_2:C_6H_3 \cdot CH(OEt) \cdot$. Similarly, simple heating with alcohol produces the changes $OMe \cdot CH_2Cl \longrightarrow OMe \cdot CH_2 \cdot OEt(\text{or Me})$. Such behaviour is limited to the halogen atom united to the carbon contiguous to the aromatic ring, halogens in other positions keeping their places; thus,

$$OMe \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot CO_2H + Et \cdot OH \longrightarrow OMe \cdot C_6H_4 \cdot CH(OEt) \cdot CHBr \cdot CO_2H.$$

The same holds with aliphatic compounds containing a halogen atom at a distance from the carbon atom united to the alkoxyl; thus, the compounds $OMe \cdot CH_2 \cdot CH_2Cl(I)$, $OEt \cdot CH_2 \cdot CH_2I$, $OMe \cdot CH_2 \cdot CBr(NO_2)_2$, and $O(CH_2 \cdot CH_2I)_2$ are so stable that some of them resist the actions of sodium, zinc, sodium acetate, and silver

acetate, whereas the compounds $O[CH_2Cl(or\ Br)]_2$ are so unstable that they decompose in moist air.

This varying behaviour of halogen atoms according to their position furnishes explanations for many reactions. The ready elimination of the halogen is regarded by Zincke and Werner as due to the formation of an intermediate oxonium or quinonic compound, thus, $OMe\cdot C_6H_4\cdot CHRBr \longrightarrow BrMe{-}O{:}C_6H_4{:}CHR$, or $OH\cdot C_6H_4\cdot CH_2Br \longrightarrow O{:}C_6H_4\cdot H(CH_2Br) \longrightarrow OH\cdot C_6H_4\cdot CH_2\cdot OEt$; an intermediate oxonium compound is probably formed in the case of the aliphatic derivatives: $OMe\cdot CH_2Br \longrightarrow BrMe{-}O{:}CH_2$. [Cf. Hoering, A., 1904, i, 577.]

Certain groups, such as the nitro and cyano residues, enhance the activity of other groups in the para-position in an aromatic nucleus. Thus, the nitrosoamine, $NPhMe\cdot NO$, exhibits indifferent behaviour and gives up the nitroso residue only with difficulty, whereas its *p*-nitro derivative, $NO_2\cdot C_6H_4\cdot NMe\cdot NO$, immediately yields diazomethane when treated with cold sodium hydroxide. Further, alkyl ethers of phenols yield their alkyl groups only as the result of energetic reactions, but if a nitroso- or an azo-group is introduced in the ortho position to the alkoxyl, the alkyl residue is easily removed with formation of the corresponding phenols: $Ph\cdot N_2\cdot C_6H_4\cdot OMe \longrightarrow Ph\cdot N_2\cdot C_6H_4\cdot OH$, and $NO\cdot C_6H_4\cdot OMe \longrightarrow NO\cdot C_6H_4\cdot OH$. Recently, Borsche and Exss (this vol., i, 218) have shown that the azo group increases the activity of halogen atoms in the ortho- or para-position, although its effect is less than that of other negative groups, such as the nitro, cyano, carbethoxy groups, etc.

In addition to the numerous examples, given earlier, of the migration of an oxygen atom from nitrogen to carbon, in aliphatic as well as in aromatic compounds, mention is made of the following, which take place under the influence of an alkali: the conversion of nitrocoumarone into an oxime, $C_6H_4<^{CH}_{O-}>C\cdot NO_2 \longrightarrow C_6H_4<^{CO}_{O-}>C{:}NOH$, and the formation of an amide,

$$N_3\cdot C_6H_4\cdot CO\cdot NH_2,$$

from the *o*-azide, $N_3\cdot C_6H_4\cdot CH{:}NOH$; the latter change is the only example of such a transposition taking place in an alkaline medium.

T. H. P.

Low-temperature Tar obtained from the Zeche Fürst Hardenberg Coal and, in particular, the Content of Benzene, Phenol, and Acetone. Reply to Broche. F. Schütz, W. Buschmann, and H. Wissebach (*Ber.*, 1924, 57, [*B*], 619—622; cf. A., 1923, i, 907).—The conflicting results obtained by Broche are due to the fact that the authors dealt with the composition of the so-called "tar benzines" (*i.e.*, the light oils obtained by dehydrating primary tar), whereas Broche mixed the "tar benzines" and the "gas benzines" together before examination. The authors confirm their previous results (cf. A., 1923, i, 195, 452) regarding the content of benzene, phenol, and acetone. H. Lange obtained 30

kg. of pure acetone on working up 120 cubic metres of tar-water; the authors do not accept Broche's suggestion that their "abnormal" results were due to overheating of the retorts. F. A. M.

Remarks on F. Fischer's Paper, "The Relation between Low-temperature Tar, Coke-oven Tar, and Petroleum." F. Schütz (*Ber.*, 1924, **57**, [*B*], 623—627; cf. A., 1923, i, 889).—Facts are quoted, such as the percentage of aromatic hydrocarbons, specific gravities, etc., to prove that Fischer's view as to the similarity between crude petroleum and low-temperature tar cannot be maintained. On the contrary, the products obtained from the low-temperature carbonisation of coal must be regarded as new types of products which cannot be compared with the great majority of natural petroleums but are of great technical importance. [Cf. also preceding abstract.] F. A. M.

Japanese Petroleum. II. S. Komatsu and N. Tanaka (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 143—146; cf. this vol., i, 502).—Petroleum from Nishiyama, Echigo, contains benzene and *n*-hexane.

Hydrogenation of Aromatic Compounds with the Aid of Platinum. VII. Decahydronaphthalene prepared using Platinum Black. R. Willstätter and F. Seitz (*Ber.*, 1924, **57**, [*B*], 683—684; cf. A., 1923, i, 771).—According to Hückel (this vol., i, 31), all preparations of decahydronaphthalene are mixtures of the *cis*- and *trans*-forms, the product obtained by the use of platinum black containing about 90% of the *cis*- and 10% of the *trans*-form. The authors have examined various preparations made with the aid of platinum and found all to have the constants (b. p. 193—193·5° corr.; d_4^{20} 0·8938—0·8942; n_D^{20} 1·4796) of the pure *cis*-form, nor could any trace of the *trans*-form be obtained on fractional distillation. Reduction of naphthalene with nickel and hydrogen at 160—162°, however, yielded chiefly the *trans*-form, d_4^{20} 0·8784; n_D^{20} 1·4729. F. A. M.

Preparation of Tetralin [Tetrahydronaphthalene]. H. Inoue (*J. Chem. Ind. Japan*, **1923**, **26**, 1316—1329).—For the hydrogenation of naphthalene, electrolytic hydrogen was used, and the nickel catalyst was prepared by electrolysing a 5—10% solution of sodium phthalate containing a slight excess of phthalic acid at 17—25°, using a nickel anode; the nickel hydroxide precipitated in the neighbourhood of the cathode is more active than that obtained by any other process. It is converted into oxide and then to metal at 310—320°. Purified naphthalene containing only 0·04% of sulphur was used and the hydrogenation was conducted in a specially designed autoclave of 7 litres capacity at 30 atm. pressure. The tetralin obtained had, after distillation, *d* 0·970. Decalin was prepared from tetralin by the same process. K. K.

Lely's Benzene Theory. J. D. van Roon (*Chem. Weekblad*, 1924, **21**, 174).—A reply to Lely's response (this vol., i, 380) to the author's criticism of the theory. S. I. L.

Electrochemical Oxidation of Aromatic Hydrocarbons. F. FICHTER (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 75—95).—A general theoretical discussion of the electrolytic oxidation of benzene derivatives, illustrated mainly by the results of the author and his collaborators. Benzene is oxidised first to phenol, then to quinol and pyrocatechol, eventually to quinone, and is finally completely disrupted. The oxidation process is governed by the following factors: (1) concentration, (2) current density, (3) nature of anode, (4) influence of cathode if no diaphragm be used, (5) nature of the electrolyte, (6) secondary reactions, *i.e.* use of a solution of a salt of a metal having a variable valency, (7) superimposition of alternating on direct current.

When phenols are oxidised, the tendency is for *p*-quinones to be formed; thus anisole gives benzoquinone, *m*-tolyl methyl ether yields toluquinone, and *m*-xylenol *p*-xyloquinone. When phenol itself is appropriately oxidised there are formed, besides the usual products, certain hydroxydiphenyls and diphenyl ethers (Fichter and Brunner, A., 1916, i, 644; Fichter and Ackermann, A., 1919, i, 586). Recent investigation, the results of which remain unpublished, has shown that guaiacol, *p*-tolyl methyl ether, and *m*-xylenol similarly yield 4 : 4′-dihydroxy-3 : 3′-dimethoxydiphenyl, 2-hydroxy-2′-methoxy-4 : 4′-dimethyldiphenyl, and 2 : 2′-dihydroxy-3 : 5 : 3′ : 5′-tetramethyldiphenyl respectively. W. A. S.

Action of Sodium Sulphite on some Trinitro Compounds and on Tetranitromethane. Purification of Tolite [2 : 4 : 6-Trinitrotoluene]. H. MURAOUR (*Bull. Soc. chim.*, 1924, [iv], **35**, 367—379; cf. A., 1922, i, 443, 1006).—Dilute solutions of sodium sulphite (3 to 5%) dissolve 2 : 3 : 4-trinitrotoluene (β) and 2 : 4 : 5-trinitrotoluene (γ) in the cold, giving colourless solutions of the corresponding sodium dinitrosulphonates, one of the adjacent ortho-nitro groups being replaced. Thus 2 : 4 : 5-trinitrotoluene is converted into sodium 2 : 4-dinitrotoluene-5-sulphonate. Symmetrical trinitrotoluene, however, only reacts slightly with dilute sodium sulphite, forming an additive product which is only stable in concentrated solutions of the sulphite and from which, on dilution, the greater part of the trinitrotoluene is precipitated. Trinitrobenzene dissolves in cold dilute sodium sulphite giving an intense red solution, from which the trinitrobenzene is precipitated unchanged on acidifying. *s*-Trinitro-*m*-xylene and trinitromesitylene do not react with aqueous sodium sulphite. Tetranitromethane reacts readily; the reaction appears to proceed in two stages, the sodium trinitromethanesulphonate first formed being subsequently hydrolysed to the sodium salt of trinitromethane.

The purification of crude commercial trinitrotoluene by the sodium sulphite process is discussed, and the application of the process to the determination of the unsymmetrical trinitrotoluenes in crude trinitrotoluene is described.

The reaction has also been utilised for the separation and approximate determination of the trinitroxylenes, the trinitro-

derivatives of *o*- and *p*-xylene reacting with dilute sodium sulphite, whilst trinitro-*m*-xylene does not. [Cf. *B.*, 1924, 451.] R. B.

Sulphonation of *p*-Cymene. M. PHILLIPS (*J. Amer. Chem. Soc.*, 1924, **46**, 686—694).—The proportions of the isomeric monosulphonic acids produced by sulphonation of *p*-cymene have been investigated using a method based on the melting-point curves of the corresponding sulphonamides. The proportion of sulphuric acid used has less effect than temperature. The best yield of the β-acid (*p*-cymene-3-sulphonic acid) is obtained using 1 part of *p*-cymene to 3 parts of sulphuric acid, sulphonating for 4 hours at 100°. Sulphonation at lower temperatures favours formation of the 2-isomeride; thus 15·6% of the 3-sulphonic acid is formed at 100° and 2·5% at 0° (using fuming sulphuric acid containing 20% of anhydride). No disulphonic acid appears to be formed at or below 50°, but increasing amounts are produced at higher temperatures. The proportion of *p*-cymene-2-sulphonic acid is somewhat increased by addition of copper or mercuric sulphate.

C. J. S.

Synthesis of Higher Homologues of *m*-Methylethylbenzene. A. MAILHE (*Bull. Soc. chim.*, 1924, [iv], **35**, 365—367).—By the action of acid chlorides on *m*-methylethylbenzene in carbon disulphide solution in the presence of aluminium chloride, followed by hydrogenation of the ketone first formed in the presence of nickel according to Darzens' method (A., 1905, i, 66), a number of higher homologues of *m*-methylethylbenzene have been obtained. The new alkyl group enters the benzene ring in the 6-position. 2-*Methyl*-4-*ethylacetophenone* has b. p. 239—240° (*semicarbazone*, m. p. 185°), 1-*methyl*-3 : 6-*diethylbenzene*, b. p. 205—207°; 2-*methyl*-4-*ethylphenyl ethyl ketone*, b. p. 250—252°; 1-*methyl*-3-*ethyl*-6-*propylbenzene*, b. p. 213—215°, d_4^{11} 0·8831; 2-*methyl*-4-*ethylphenyl* iso*propyl ketone*, m. p. 132°, b. p. 258—259°, d_4^{11} 0·9557; 1-*methyl*-3-*ethyl*-6-iso*butylbenzene*, b. p. 228—229°, d_4^{11} 0·8863; 2-*methyl*-4-*ethylphenyl propyl ketone*, b. p. 265—266°; 1-*methyl*-3-*ethyl*-6-*butylbenzene*, b. p. 236—237°, d^{11} 0·6882(?); 2-*methyl*-4-*ethylphenyl* iso*butyl ketone*, b. p. 274°; 1-*methyl*-3-*ethyl*-6-iso*amylbenzene*, b. p. 245—246°, d^{11} 0·8801. By the action of benzoyl chloride on *m*-methylethylbenzene in the presence of aluminium chloride 2-*methyl*-4-*ethylbenzophenone*, b. p. 318—320°, was obtained, which on hydrogenation was converted into 2-*methyl*-4-*ethyldiphenylmethane*, b. p. 298—300°, d^{11} 1·0141. R. B.

Alkylation of Primary Amines with Aluminium Alkoxides to give Secondary Amines Free from Tertiary Amines. W. A. LAZIER and H. ADKINS (*J. Amer. Chem. Soc.*, 1924, **46**, 741—746).—Both aromatic and aliphatic primary amines may be alkylated by heating with aluminium alkoxide in sealed tubes at 250—350°. Aniline with aluminium ethoxide yielded a colourless reaction product containing 94% of ethylaniline and 6% of aniline. Other secondary amines were prepared in good yield by alkylating aniline, *p*-toluidine, and *n*-amylamine, but the opti-

mum conditions have not yet been ascertained. The yields obtained, using acetanilide in place of aniline, were considerably lower. These results do not support Nef's dissociation hypothesis (A., 1901, i, 626), by which he explained the mechanism of alkylation.

C. J. S.

Highly Chlorinated Hydroaromatic Products containing Nitrogen. DURAND und HUGUENIN A.-G. (Brit. Pat. 198676).—Amines containing negative substituents are chlorinated, in the absence of moisture, without previously protecting the amino group by salt formation, as is necessary in the case of the unsubstituted amines (cf. Brit. Pat. 193843). For example, chlorine is introduced into an ice-cooled solution of 20 g. of 2 : 5-dichloroaniline in 600 c.c. of chlorobenzene. The paste initially formed having become fluid, the mixture is heated at about 100°, filtered, and the chlorobenzene distilled under diminished pressure. A crystalline compound (containing eight chlorine atoms) separates, which crystallises from light petroleum in colourless laminæ, m. p. 125°.

W. T. K. B.

Nitration of *p*-Bromoacetanilide. R. H. GRIFFITH (*J. Chem. Soc.*, 1924, **125**, 940—941).—The nitration of *p*-bromoacetanilide at 10° with excess of nitric acid and sulphuric acid yields 2 : 4-dibromo-6-nitroacetanilide, m. p. 215°, 4-bromo-2 : 6-dinitroacetanilide, and 4-bromo-2-nitroacetanilide. 2 : 4-Dibromoacetanilide nitrated with excess of fuming nitric acid yields 2 : 4-dibromo-6-nitroacetanilide, which is hydrolysed to 2 : 4-dibromo-6-nitroaniline, m. p. 128°, with alcoholic hydrochloric acid. Nitration in the presence of sulphuric acid yields 2 : 4-dibromo-5-nitroacetanilide, m. p. 172°. 4-Bromo-2 : 6-dinitroaniline melts at 162°.

R. B.

Electrolytic Preparation of Metanilic Acid and its Commercial Possibilities. A. K. DOOLITTLE (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 43—62).—In only one particular is the electrolytic reduction of *m*-nitrobenzenesulphonic acid likely to be more advantageous than the usual iron reduction, and that is that the former process might be made continuous. The author has therefore investigated the electrolytic method, using lead electrodes and 10% sulphuric acid as electrolyte. To the cathode solution, contained in a porous vessel, pure calcium *m*-nitrobenzenesulphonate was added. Reduction did not take place at 24°. The best results were obtained at 70°, with a bright lead cathode, current density 0·585 amp. per sq. dm., and cathode solution 1%. The yield was 67% of theory and current efficiency 64%. [Cf. *B.*, 1924, 288.]

W. A. S.

Crystallographic Investigation of *p*-ββ-Dimethylpropylbenzenesulphanilide and Benzyltrimethylsilicane-*p*-sulphanilide. N. ZENZÉN (*Arkiv Kem., Min., Geol.*, 1923, **8**, No. 34, 1—10).—*p*-ββ-Dimethylpropylbenzenesulphanilide,

$$CMe_3 \cdot CH_2 \cdot C_6H_4 \cdot SO_2 \cdot NHPh$$

(cf. Bygdén, A., 1920, i, 478), crystallises in holohedral monoclinic

crystals, $a:b:c=0{\cdot}6869:1:0{\cdot}7536$, $\beta=113°\ 17'$, and benzyltrimethylsilicane-*p*-sulphanilide, $SiMe_3{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHPh$ (cf. Bygdén, A., 1918, i, 134), also in holohedral monoclinic crystals, $a:b:c=0{\cdot}6973:1:0{\cdot}7698$, $\beta=113°\ 38'$. True mixed crystals of these two compounds are formed. The axial angle usually has appreciably different values at the two sides of a mixed crystal, probably on account of its zonal structure. T. H. P.

Decomposition of Quaternary Ammonium Hydroxides. J. v. Braun and R. S. Cahn (*Annalen*, 1924, **436**, 262—273; cf. A., 1911, i, 610).—The decomposition of β-phenylethyltrimethylammonium hydroxide giving a quantitative yield of styrene and a tertiary base has been applied to the synthesis of tertiary bases previously difficult to obtain. By the action of β-phenylethylamine on ethyl αα′-dibromoadipate in chloroform solution are obtained *ethyl β-phenylethylpyrrolidine-2 : 5-dicarboxylate*, oil, b. p. 212—214°/14 mm. (*chloroplatinate*, decomp. 160—161°), and ethyl αα′-di(β-phenylethylamino)adipate,

$$[CO_2Et{\cdot}CH(NH{\cdot}CH_2{\cdot}CH_2Ph)CH_2{\cdot}]_2,$$

a thick oil; the free acid, $C_{22}H_{28}O_4N_2$, forms long, colourless needles, m. p. 118°. *1-β-Phenylethylpyrrolidine-2 : 5-dicarboxylic acid*, colourless crystals, decomp. 215° (*hydrochloride*, m. p. 177—178°), on dry distillation gives 1-β-phenylethylpyrrolidine, a mobile oil, b. p. 138—139°/21 mm. (*picrate*, m. p. 139—140°, *methiodide*, m. p. 143°). The methiodide on treatment with silver oxide and distillation of the quaternary ammonium hydroxide gives 60% of the theoretical yield of styrene and 1-methylpyrrolidine, b. p. 78°. Reduction of ethyl 1-β-phenylethylpyrrolidine-2 : 5-dicarboxylate with sodium and alcohol yields *1-β-phenylethyl-2 : 5-dihydroxymethylpyrrolidine*, a viscous, colourless oil, b. p. 225°/13 mm. (*hydrochloride*, m. p. 127—129°, *picrate*, m. p. 108—111°, *methiodide*, oily), but the yield is small and no attempt was made to convert it into the corresponding 1-methylpyrrolidine.

β-Phenylethyldimethylamine reacts readily with *o*-xylylene bromide (for the preparation of which a new method from *o*-toluidine is described), in chloroform solution, yielding the *diquaternary bromide*, $C_{28}H_{38}N_2Br_2$, colourless crystals, m. p. 206°, which on treatment with silver oxide and distillation gives 65% of the theoretical yield of styrene and 60% of tetramethyl-*o*-xylylenediamine, $C_6H_4(CH_2{\cdot}NMe_2)_2$, colourless oil, b. p. 105—106°/14 mm. [*picrate*, m. p. 187—188°, *methiodide*, m. p. 219° (decomp.)].

β-Phenylethyldimethylamine and αε-dibromopentane react readily at water-bath temperature, giving the *diquaternary bromide*, $CH_2(CH_2{\cdot}CH_2{\cdot}NMe_2Br{\cdot}CH_2{\cdot}CH_2Ph)_2$, m. p. 121°, which on conversion into the hydroxide and distillation gives 60% of the theoretical yield of styrene and 25% of tetramethylpentamethylenediamine. R. B.

Tenacity of Organic Residues. II. J. v. Braun and H. Engel (*Annalen*, 1924, **436**, 299—320; cf. A., 1923, i, 1193).—Further experiments have been undertaken to test the relative firmness of attachment of groups of the benzyl and allyl type to

nitrogen and to halogen. By decomposition of appropriate tertiary bases with cyanogen bromide, it is shown that the introduction of the groups Me, Et, Ph, respectively, into the para-position in the benzyl radical diminishes in the order named the firmness with which the substituted benzyl group is attached to nitrogen. A similar result was obtained from experiments in the allyl series with the radicals allyl, crotonyl, and cinnamyl. The affinity of the radicals for nitrogen (and also for carbon) accordingly stands in the order Me<Et<Ph, and the same order holds in regard to chlorine. These results are at variance with those of Meerwein (A., 1920, i, 2) and Skraup (A., 1919, i, 598; 1922, i, 574), but the order Ph<*p*-C_6H_4Me·<*p*-C_6H_4Et·<*p*-C_6H_4Ph· is in accordance with Skraup's observations and those of Schlenk on the dissociation of hexa-arylethanes. A comparison of the allyl and benzyl series shows that in regard to nitrogen the radicals can be arranged in the following order of diminishing affinity: CH_2Ph–, CH_2:CH·CH_2–, $CHMe$:CH·CH_2–, $CHPh$:CH·CH_2–, *p*-C_6H_4Me·CH_2–, *p*-C_6H_4Et·CH_2–, *p*-C_6H_4Ph·CH_2–, methylation of the benzyl residue in the para-position decreasing the firmness of its attachment to nitrogen more than phenylation of the allyl residue. Similar results were obtained by studying the reaction of benzyl, *p*-methylbenzyl, *p*-ethylbenzyl, and *p*-phenylbenzyl chlorides with sodium ethoxide.

p-*Ethylbenzyl alcohol*, b. p. 115—117°/9 mm., was obtained by the action of potassium hydroxide on the corresponding aldehyde, prepared by Gattermann's method (A., 1897, i, 519), and with hydrochloric acid was converted into p-*ethylbenzyl chloride*, b. p. 81—82°/11 mm. p-*Phenylbenzyl chloride*, m. p. 68°, is similarly prepared through p-*phenylbenzyl alcohol*, m. p. 101—102°, b. p. 183—184°/11 mm., from *p*-phenylbenzaldehyde (obtained from diphenyl by Gattermann's method), or alternatively from *p*-phenylbenzonitrile by catalytic reduction to p-*phenylbenzylamine*, colourless crystals, m. p. 127—128° (*hydrochloride*, sparingly soluble, m. p. 282°; *picrate*, m. p. 205°; *acetyl* derivative, m. p. 180°; *benzoyl* derivative, m. p. 162°; *phenylthiocarbamide*, m. p. 150°; *methiodide*, m. p. 221°), and conversion of the amide into the alcohol by the diazo reaction. The secondary base, *di*-p-*phenylbenzylamine*, m. p. 132° (*hydrochloride*, m. p. above 300°, *nitroso* compound, m. p. 170°), is also formed in the reduction.

Benzylmethylamine (obtained by catalytic reduction of benzylidenemethylamine with nickel at 100°) with *p*-methylbenzyl chloride yields *benzyl*-p-*methylbenzylmethylamine*, colourless liquid, b. p. 160°/11 mm. (*methiodide*, m. p. 190°), which is converted by cyanogen bromide into a quaternary *salt*, probably *benzyldi*-p-*methylbenzylmethylammonium bromide*, m. p. 184°, p-*methylbenzyltrimethylammonium bromide*, m. p. 170—175°, and benzylmethylcyanamide, b. p. 139—140°/12 mm. In a similar manner *benzyl*-p-*phenylbenzylmethylamine*, m. p. 44°, b. p. 190—192° (*hydrochloride*, m. p. 187°; *picrate*, m. p. 146°; *methiodide*, m. p. 162°), is obtained and transformed by cyanogen bromide into an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, m. p. 200°, and benzylmethylcyanamide.

p-*Methylbenzylmethylamine*, b. p. 83°/11 mm. (*hydrochloride*, m. p. 174°; *picrate*, m. p. 145°), was obtained by reduction of the Schiff's base from *p*-tolualdehyde and methylamine with sodium and alcohol. With *p*-ethylbenzyl chloride this yields the tertiary base, p-*methylbenzyl*-p-*ethylbenzylmethylamine*, b. p. 181°/9 mm., which on treatment with cyanogen bromide yields the quaternary salt, $C_6H_4Me{\cdot}CH_2{\cdot}NMe(CH_2{\cdot}C_6H_4Et)_2Br$, m. p. 168°; *p*-ethylbenzyltrimethylammonium bromide (chloroplatinate, m. p. 216°), and *p*-methylbenzylmethylcyanamide. p-*Methylbenzyl*-p-*phenylbenzylmethylamine*, b. p. 253—255°/13 mm., was similarly obtained from *p*-phenylbenzyl chloride, and this base by treatment with cyanogen bromide yields an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, m. p. 200°, and a substance, m. p. 70°, containing bromine, probably formed by the action of cyanogen bromide on the primarily formed *p*-methylbenzylmethylcyanamide. In a similar way p-*methylbenzylmethylbutenylamine*,

$$C_6H_4Me{\cdot}CH_2{\cdot}NMe{\cdot}CH_2{\cdot}CH{:}CHMe,$$

b. p. 116—118°/11 mm., is obtained by the action of crotonyl bromide on p-*methylbenzylmethylamine*, and this base is transformed by cyanogen bromide into an oily quaternary compound, *p*-methylbenzyltrimethylammonium bromide (m. p. 184°), and *methylcrotonylcyanamide*, $CHMe{:}CH{\cdot}CH_2{\cdot}NMe{\cdot}CN$, b. p. 92—93°/55 mm.

p-*Methylbenzylcinnamylmethylamine*, b. p. 218—220°/12 mm., is decomposed by cyanogen bromide with production of an oily quaternary salt, *p*-methylbenzyltrimethylammonium bromide (m. p. 194°), and cinnamylmethylcyanamide.

p-*Ethylbenzylmethylamine*, b. p. 105°/10 mm., obtained by the action of *p*-ethylbenzyl chloride on methylamine, reacts with *p*-phenylbenzyl chloride, yielding p-*phenylbenzyl*-p-*ethylbenzylmethylamine*, b. p. 255—257°/11 mm. (*hydrochloride*, m. p. 205°), which on decomposition with cyanogen bromide gives an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, and *p*-ethylbenzylmethylcyanamide.

p-*Phenylbenzylmethylamine*, b. p. 173—174°/11 mm., was obtained by condensing *p*-phenylbenzaldehyde with methylamine and reducing the Schiff's base (m. p. 51°) with sodium. With cinnamyl bromide, it yields an oily quaternary compound which on distillation in a vacuum yields a tertiary *base*, $C_{23}H_{23}N$ (*hydrochloride*, m. p. 224°), which is converted by cyanogen bromide into an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide (m. p. 198°), and cinnamylmethylcyanamide.

Cinnamylmethylamine is a mobile liquid, b. p. 110—112°/12 mm. With allyl bromide it yields *cinnamylmethylallylamine*, $CHPh{:}CH{\cdot}CH_2{\cdot}NMe{\cdot}CH_2{\cdot}CH{:}CH_2$, b. p. 166—168°/11 mm., which on decomposition with cyanogen bromide yields an oily quaternary compound (*chloroplatinate*, $C_{44}H_{52}N_2{\cdot}Cl_6Pt$, m. p. 85°), cinnamyltrimethylammonium bromide (m. p. 165°), and *methylallylcyanamide*, $CH_2{:}CH{\cdot}CH_2{\cdot}NMe{\cdot}CN$. Similarly from cinnamylmethylamine and crotonyl chloride is obtained *cinnamylmethylcrotonylamine*, b. p. 180—182°/10 mm., from which the quaternary *salt*, $(CHPh{:}CH{\cdot}CH_2)_2NMe(CH_2{\cdot}CH{:}CHMe)Br$, m. p. 79°, cinn-

amyl bromide, and methylcrotonylcyanamide are formed on treatment with cyanogen bromide. R. B.

Catalytic Reduction of Phenol and α-Naphthol under High Pressure. H. INOUE (*J. Chem. Ind. Japan*, 1923, **26**, 1330—1334; cf. this vol., p. 628).—By the same method as that used in the catalytic preparation of tetralin, phenol was reduced at about 200° to *cyclo*hexanol (b. p. 135°, d^{20} 0·9547, n_D^{20} 1·4650), and α-naphthol to a mixture of tetralin (46·6%), *ar*-tetrahydro-α-naphthol (40·9%), and α-ketotetrahydronaphthalene (12·5%). K. K.

Esterification of *cyclo*Hexanol and some of its Homologues. (MLLE.) G. CAUQUIL (*Compt. rend.*, 1924, **178**, 1538—1540; cf. this vol., i, 280).—On heating 2-, 3-, and 4-methyl*cyclo*hexanol with acetic acid, 49·8%, 53·1%, and 54·1%, respectively, of the three alcohols has undergone esterification at equilibrium, showing a decrease of 5·8, 2·5, and 1·5%, compared with *cyclo*hexanol. For 3 : 4-dimethyl*cyclo*hexanol the corresponding decrease is 8·1 and for 2-ethyl*cyclo*hexanol, 6·4%. J. W. B.

Preparation of Stereoisomerides in the Disubstituted *cyclo*Hexanol Series. M. GODCHOT and P. BEDOS (*Compt. rend.*, 1924, **178**, 1184—1186).—The action of hypochlorous acid on Δ^3-methyl*cyclo*hexene results in the formation of a mixture of two isomerides of 4-*chloro*-1-*methyl*cyclo*hexan*-3-*ol*. These were separated by repeated fractionations, and the two fractions were converted by the Grignard reaction into two 1 : 4-*dimethyl*cyclo*hexan*-2-*ols*, yielding *allophanates* of m. p. 158° and 125°, respectively. The alcohols on regeneration from these esters were colourless liquids, b. p. 175°/760 mm., d^{17} 0·9066, n_D^{17} 1·4521, and b. p. 177°/760 mm., d^{17} 0·9079, n_D^{17} 1·4544, respectively. On oxidation with chromic acid, both alcohols give 1 : 4-*dimethyl*-cyclo*hexan*-2-*one*, b. p. 171—172°; *semicarbazone*, m. p. 122°. H. J. E.

Auto-oxidation and Anti-oxygens. Catalytic Properties of Iodophenols. C. MOUREU, C. DUFRAISSE, and J. P. DES TOUCHES (*Compt. rend.*, 1924, **178**, 1497—1501; cf. A., 1922, i, 250; 1923, ii, 308).—The inhibiting action on the auto-oxidation of acraldehyde of substances containing both a phenolic group and iodine in the same molecule has been studied. Within the limits of experimental error, neither exaltation nor diminution in the activity of the phenol group occurs. Thus *o*-iodophenol exhibits a very slight diminution in activity compared with phenol itself. The very slight activity of iodobenzene shows that iodine in the nucleus has very little effect; but the introduction of a second phenolic group in the *o*-position (pyrocatechol) increases the activity coefficient 200 times. The activities of 2 : 6- and 3 : 4-di-iodophenol, and 2 : 4 : 6-tri-iodophenol are only slightly greater than that of phenol itself, and in equal molecular concentration 2 : 6-di-iodoquinol has the same activity as quinol. The dimethyl ether of monoiodoquinol has the same activity as quinol

dimethyl ether, each exhibiting an initial retarding effect followed by a distinct acceleration of the auto-oxidation. J. W. B.

Nitration. II. Mononitration of Phenol. F. ARNALL (*J. Chem. Soc.*, 1924, **125**, 811—816; cf. *ibid.*, 1923, **123**, 3111).—Nitration of phenol in an organic solvent gives much better results than in aqueous solution, but the velocity of nitration depends on the nature of the solvent. At 10°, reaction in acetic anhydride containing 10% of nitric acid is apparently instantaneous. In acetone, nitration with 10% nitric acid proceeds to the extent of 80% in 3 hours; in ether, 68% in 12 hours; in alcohol (2 parts) and acetic acid (1 part), 75% in 48 hours; in absolute alcohol, 55% in 48 hours. The relative proportions of the isomerides are independent of the solvent. The best results were obtained with glacial acetic acid, without formation of tar, the yield being almost quantitative at temperatures up to 50°. Raising the temperature of nitration or increasing the concentration of the nitric acid slightly increases the proportion of *o*-nitrophenol formed. The best yields of the mononitrophenols were obtained with 10% nitric acid at 25°. The mixture of mononitrophenols was analysed by a method involving steam distillation of the *o*-nitrophenol and thermal analysis of the benzyl ethers of *m*- and *p*-nitrophenol.

The following derivatives of *m*-nitrophenol have been obtained: *acetate*, m. p. 55—56°; *picrate*, m. p. 170—171°; *benzyl ether*, m. p. 55°; *acetonyl ether*, m. p. 83—84°; acetophenonyl ether, m. p. 127°. R. B.

Action of Bromine on Methyl Esters of Phenolsulphonic Acids. Determination of Sulphur in Phenolsulphonic Esters and Salts. L. J. SIMON and M. FRÈREJACQUE (*Compt. rend.*, 1924, **178**, 1282—1284).—The action at a low temperature of bromine (1 atom) on methyl *o*-cresolsulphonate in methyl-alcoholic solution, yields (1) the *methyl bromo-o-cresolsulphonate*, m. p. 143°, which retains the methylating properties of the original compound and gives, in particular, the characteristic derivative of hexamethylenetetramine (cf. this vol., i, 665), and (2) the corresponding bromo-*o*-cresolsulphonic acid. At 100° a second bromine atom enters the nucleus, from which it displaces the sulphonic group, so that, if excess of bromine is employed, the sole products of the reaction are dibromo-*o*-cresol and sulphuric acid. Similar products are obtained from methyl anisole-*p*-sulphonate, which also takes up a second bromine atom only by elimination of the sulphonic group.

Methyl sulphate, which sulphonates the phenols so readily, has no action on their bromo derivatives, even at higher temperatures (cf. A., 1923, i, 462, 1098). This inertness is in harmony with the total elimination of the sulphonic group by bromine, which allows of the use of the latter for the determination of the sulphur in sulphonic derivatives of phenols. Desvergnes' method (A., 1920, ii, 563) gives satisfactory results with the methyl esters of various phenolsulphonic acids, and with the water-soluble additive products of

the sulphonic esters with tertiary bases. No sulphuric acid is, however, liberated from the acyclic methanesulphonic and sulphoacetic acids. [Cf. *B.*, 1924, 444.] T. H. P.

Ultra-violet Absorption Spectra of Eugenol. G. THOMPSON (*J. Chem. Soc.*, 1924, **125**, 962; cf. *ibid.*, 1923, **123**, 1594).—The absorption spectrum of eugenol in thin films agrees closely with its spectrum in alcoholic solution, and the absorption bands previously recorded are therefore characteristic of the substance itself. Extinction coefficients could not be calculated, as it was not possible to measure the thickness of the films. R. B.

Catalytic Action. V. Catalytic Reduction of α- and β-Naphthyl Methyl Ethers. S. KOMATSU and S. KUMAMOTO (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 135—142).—The catalytic reduction of α-naphthol has previously been found to yield products containing *ar*- and *ac*-compounds in the ratio 1 : 9 (A., 1923, i, 782), whereas the presence of the amino group in α-naphthylamine favours the formation of *ar*-derivatives, the ratio of *ar*- to *ac*-compounds being 9 : 1. When α-naphthyl methyl ether is reduced by means of hydrogen and reduced nickel at 200°, the molecular ratio of *ar*- to *ac*-compounds is 19 : 81. β-Naphthyl methyl ether forms *ac*-derivatives less readily than does the α-ether, the molecular ratio of *ar*- to *ac*-products being 37 : 63. When reduced with sodium and boiling amyl alcohol, α- and β-naphthyl methyl ethers yield only *ar*-tetrahydronaphthyl ethers, but when β-naphthyl methyl ether is reduced with sodium and ethyl alcohol, β-*ar*-dihydronaphthyl methyl ether is obtained. C. J. S.

Preparation of 2- and 4-Nitro-α-naphthols. H. H. HODGSON and E. KILNER (*J. Chem. Soc.*, 1924, **125**, 807—811).—The 2- and 4-nitro compounds obtained by the nitration of aceto-α-naphthalide (cf. A., 1886, 754; T., 1905, **87**, 928) can be easily separated by hydrolysing the mixture with boiling 5% sodium hydroxide, and distilling the acidified solution with steam, whereby 2-nitro-α-naphthol is removed. The mixture was thus found to contain the 2- and 4-nitroaceto-α-naphthalides in the proportion 1 : 3. The poor yields of 2-nitro-α-naphthol obtained in the oxidation of 2-nitroso-1-naphthol with dilute nitric acid (A., 1892, 861) are due to the action of nitrous acid, liberated during the reaction, on the nitronaphthol. 4-Nitro-α-naphthol is attacked more rapidly than the 2-nitro compound. The addition of carbamide to the oxidation mixture raises the yield of 2-nitro-α-naphthol to 50% of the theoretical. Better results were obtained by using 100 vol. hydrogen peroxide, the yield being 50—60%. The by-products are soluble derivatives of phthalic acid. Ammonium 2-nitro-α-naphthoxide, in contrast with the nitronaphthol itself, can be distilled in steam without resinification. R. B.

Manufacture of G-Acid [β-Naphthol-6 : 8-disulphonic Acid], using Fuming Sulphuric Acid. T. KAWAGUCHI (*J. Chem. Ind. Japan*, 1923, **26**, 1233—1256).—When 1 part of β-naphthol is sulphonated with 5 parts of fuming sulphuric acid containing

20% of sulphur trioxide at 20—25° during 8 hours, G acid is the principal product, with β-naphthol-3 : 6-disulphonic acid (R acid) and -6-sulphonic acid (Schäffer acid) as by-products. Separating the last by partial crystallisation as barium salt, and G and R acids through the difference in solubility of their sodium salts in aqueous alcoholic solution, 2 grams of barium salt of Schäffer acid, 61 grams of sodium salt of G acid, and 22 grams of sodium salt of R acid were isolated from 50 grams of β-naphthol. Neglecting Schäffer acid, if G and R acids are separated as acid potassium and sodium salts, the yields of the two salts are 75 grams and 17 grams, respectively, from the same amount of β-naphthol.

K. K.

So-called Auxochromes and their Method of Action. A. Hantzsch (*Annalen*, 1924, **436**, 321—323).—A defence of the author's theory of isomeric change, in reply to Kaufmann (A., 1924, i, 37). R. B.

Reaction of Resorcinol and of Phloroglucinol with Formaldehyde. A. Zamparo (*Boll. Chim. Farm.*, 1924, **63**, 161—164).—Resorcinol and phloroglucinol are the only ordinary phenolic compounds which react immediately in the cold to give coloured precipitates when 0·1 g. is dissolved in 3 c.c. of 95% alcohol and the solution is treated successively with 2 c.c. of 40% formaldehyde solution and 3 c.c. of concentrated hydrochloric acid; the two naphthols and thymol give precipitates soluble in alcohol. [Cf. *B.*, 1924, 445.] T. H. P.

Dyes of the Aurin Type. II. H. Baines and J. E. Driver (*J. Chem. Soc.*, 1924, **125**, 907—910; cf. *ibid.*, 1923, **123**, 1214).—By the action of chloroform vapour on dry potassium phenoxide at 110° in the absence of oxygen, triphenyl orthoformate, m. p. 75°, and leucaurin, $CH(C_6H_4OH)_3$, are produced. The reaction proceeds more slowly with boiling chloroform, but the yield is greatly diminished by the presence of water and is not appreciably increased by using alcohol as solvent. R. B.

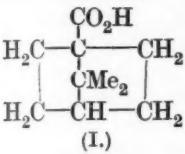
Catalytic Preparation of Benzyl Ethers. J. B. Senderens (*Compt. rend.*, 1924, **178**, 1412—1415).—The method previously described (this vol., i, 40) has now been applied to the preparation of benzyl ether, and of the mixed benzyl ethyl, benzyl propyl, benzyl *iso*propyl, benzyl butyl, benzyl *iso*butyl, and benzyl *iso*amyl ethers. For these mixed ethers, the boiling point rises, but the density diminishes as the molecular weight increases.

T. H. P.

Chemical Nature of the Naphthenic Acids. O. Aschan (*Ber.*, 1924, **57**, [*B*], 636—637).—A reply to a paper by Zelinsky and Pokrowskaja (this vol., i, 387) criticising work done by the author in 1892 (A., 1893, i, 209). The heptanaphthenecarboxylic acid was obtained pure by redistilling the methyl ester 30 times and boiled within 2°; it was probably purer than that obtained

by Zelinsky and Pokrowskaja. The author had suggested in 1892 that the naphthenic acids, $C_7H_{12}O_2$ and $C_8H_{14}O_2$, were *cyclo*pentane derivatives; the suggestions of Zelinski and Pokrowskaja are therefore not novel. F. A. M.

Ketopinic Acid. Conversion into Norcamphane-1-carboxylic Acid. E. WEDEKIND [with C. WEINAND] (*Ber.*, 1924, **57**, [*B*], 664—666).—Ketopinic acid (cf. Wedekind, Schenk, and Stüsser, A., 1923, i, 346) is converted into its *semicarbazone*, m. p. 226°, which is transformed by sodium ethoxide and ethyl alcohol at 170—180° into *norcamphane-1-carboxylic acid* (I), m. p. 221—222°; the *copper*, *lead*, *mercury*, *silver*, and *zinc* salts are described. The *calcium* salt is particularly characteristic.


(I.)

The *phenylhydrazide*, m. p. 140°, and the *amide*, m. p. 192·5°, of ketopinic acid are described. The acid is associated to a considerable degree in benzene even in dilute solution. H. W.

Catalytic Action. VI. Catalytic Action of Reduced Copper on Acid Amides. S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 157—159).—The suggestion that at a high temperature reduced copper causes simultaneous dehydration and hydration has been confirmed by passing menthon*iso*oxime over the catalyst at 200°, whereby menthonitrile and decenoic acid were obtained. Benzamide when passed over reduced copper at 250° gives benzonitrile and benzoic acid, whilst acetamide (at 200°) yields acetonitrile and acetic acid. C. J. S.

Condensation of Nitriles with Thioamides. II. Acetonitrile with Thiobenzamide, and Benzonitrile with Thioacetamide. S. ISHIKAWA (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 93—98; cf. A., 1921, i, 728).—The combination of acetonitrile and thiobenzamide, induced by saturating their ethereal solution with dry hydrogen chloride, yields, not acetimino*iso*benzamide, but benzimino*iso*thiobenzamide. The fact that thioacetamide is found in the resulting solution indicates that the acetonitrile and thiobenzamide first condense similarly to benzonitrile and thiobenzamide, and that the condensation product is unstable and decomposes into benzonitrile and thioacetamide: $CH_3{\cdot}CN+NH{:}CPh{\cdot}SH \longrightarrow NH{:}CMe{\cdot}N{:}CPh{\cdot}SH \longrightarrow NH{:}CMe{\cdot}SH+C_6H_5{\cdot}CN$; equilibrium is reached when about 20% of the reacting compounds is converted into the final products. From benzonitrile and thioacetamide, benzimino*iso*thiobenzamide and thiobenzamide were obtained, the latter product representing about 71% of the benzonitrile. T. H. P.

Electrolytic Oxidation of *p*-Nitrotoluene and *p*-Chlorotoluene to their respective Acids. R. DUNBROOK and A. LOWY (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 97—117).—Using 20% nitric acid as the electrolyte and platinum electrodes, *p*-nitrotoluene and *p*-chlorotoluene were oxidised to *p*-nitrobenzoic and *p*-chloro-

benzoic acids, respectively. In the first case, the best conditions were with a current density of 4 amp. per sq. dm., at 100°, a current efficiency of 34·1% being obtained. In the second case, the current density was 0·5 amp. per sq. dm. and the current efficiency was 65%, but with acetic acid as solvent it rose to 96%. [Cf. *B.*, 1924, 444.] W. A. S.

[*p*-Aminobenzoic] **Esters of Substituted Aminopropyl Alcohol.** W. SCHULEMANN, L. SCHÜTZ, and K. MEISENBURG (U. S. Pat. 1474567).—dl-γ-*Dimethylamino*-αβ-*dimethylpropyl* p-*aminobenzoate* (crystalline *hydrochloride*) has m. p. 81—82°. dl-γ-*Diethylamino*-αβ-*diethylpropyl* p-*aminobenzoate hydrochloride* has m. p. 146°. γ-*Diethylamino*-β-*methyl*-α-*ethylpropyl* p-*aminobenzoate hydrochloride* has m. p. 178°. CHEMICAL ABSTRACTS.

Synthetic Anæsthetics [**Alkylaminoalkyl *p*-Aminobenzoates.** E. H. VOLWILER and R. ADAMS (U.S. Pat. 1476934).—γ-*Butylallylaminopropyl* p-*aminobenzoate hydrochloride* forms white needles, m. p. 147°. *Butylallylamine*, from butyl bromide and allylamine, has b. p. 132—133°/760 mm. β-*Butylallylaminoethyl* p-*aminobenzoate hydrochloride* has m. p. 184°. The *hydrochlorides* of *propylallylaminopropyl* and iso*propylallylaminopropyl* p-*aminobenzoates* are viscous oils. iso*Amylallylaminoethyl alcohol*, b. p. 132—133°/55 mm. (obtained by heating ethylene oxide with *iso*amylallylamine at 60°) yields a p-*aminobenzoate hydrochloride*, m. p. 194—195°. CHEMICAL ABSTRACTS.

Identity of Abietic Acids Extracted from Different Colophonies. G. DUPONT and R. UZAC (*Bull. Soc. chim.*, 1924, [iv], **35**, 394—404; cf. Schulz, *Mon. Sci.*, 1920, **10**, 109).—Crude abietic acid, obtained by extracting colophony with 95% alcohol and hydrochloric acid, was purified by crystallisation to a constant rotatory power. In this way, pure abietic acid of m. p. 173°, and [α] −105° for the yellow light of the mercury arc, was obtained from colophony from the following sources: (1) *Pinus maritima*; (2) Aleppo pine; (3) *P. Laricio austriaca*; (4) *P. longifolia*; (5) *P. pinea*. Pimaric acid (A., 1921, i, 510), α- and β-alepic acids, and the sapinic acids are easily isomerised to abietic acid (β-pimarabietic acid) by the influence of hydrochloric acid. For these reasons, the authors do not regard abietic acid as a constituent of the natural gums, but as the final stable isomeric form of the constituents of these gums. The suggestion of Knecht and Hibbert (cf. A., 1919, i, 338) that abietic anhydride forms a constituent of colophony is rejected because abietic acid has been obtained from colophony in dry tubes at 130°, when no water was present to convert the anhydride into acid, and because abietic acid can be obtained from molten colophony in the presence of hydrogen chloride by merely seeding with a small quantity of the acid. It is suggested that the isomerisation of *l*-pimaric, α-sapinic, and β-sapinic acids takes place in two stages under the action of heat or hydrochloric acid, α-pimarabietic acid and α- and β-sapinabietic acids being formed intermediately. *d*-Pimaric acid is not isomerised under these conditions. R. B.

ααβ-Triphenylpropionic Acid and some of its Derivatives. (MLLE.) P. RAMART (*Bull. Soc. chim.*, 1924, [iv], **35**, 196—200).—A more detailed account of work already published (this vol., i, 171). S. K. T.

Calcium *o*-Benzyloxybenzoate. E. A. WILDMAN (U.S. Pat. 1481779).—Saponification of the product obtained by the interaction of methyl salicyate, benzyl chloride, and sodium ethoxide yields *o*-benzyloxybenzoic acid, m. p. 75°. The *calcium* salt, $Ca(O{\cdot}CO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2Ph)_2$, is obtained by boiling the acid with water and calcium carbonate.

A New Iodosalicylic Acid. P. BRENANS and C. PROST (*Compt. rend.*, 1924, **178**, 1010—1012; cf. A., 1923, i, 797).—*4-Iodosalicylic acid*, colourless needles, turning brown at 200°, m. p. 228° (decomp.), was prepared from 4-nitro-*o*-toluidine by acetylation, oxidation to 4-nitroacetylanthranilic acid, deacetylation, and diazotisation to 4-nitrosalicylic acid, the ethyl ester of which was reduced; from the diazonium sulphate of the resulting amino compound hydriodic acid yielded *ethyl* 4-*iodosalicylate* (needles, m. p. 21°), which was hydrolysed. The *acetyl* derivative of the acid forms colourless crystals, m. p. 156°. H. J. E.

Iodinated *m*-Hydroxybenzoic Acids. P. BRENANS and C. PROST (*Compt. rend.*, 1924, **178**, 1285—1287).—Certain of the results obtained by the authors have been already published by Beyer (A., 1922, i, 37). The iodo-*m*-hydroxybenzoic acid, m. p. 226° (decomp.), prepared by Weselsky's method (A., 1875, 139) is identical with that obtained from 4-amino-*m*-hydroxybenzoic acid by way of the diazo compound, and is, therefore, 4-iodo-*m*-hydroxybenzoic acid. *4-Iodo*-m-*acetoxybenzoic acid* forms white crystals, m. p. 203°.

The iodohydroxybenzoic acid prepared from the amino-*m*-hydroxybenzoic acid obtained when 6-benzeneazo-*m*-hydroxybenzoic acid is reduced by means of stannous chloride and hydrochloric acid, is identical with that prepared from Griess' nitro-*m*-hydroxybenzoic acid (A., 1887, 485), which is hence the 6-nitro-acid. [Cf. Beyer, *loc. cit.*] T. H. P.

A New Iodo-*p*-hydroxybenzoic Acid. P. BRENANS and C. PROST (*Compt. rend.*, 1924, **178**, 1555—1557; cf. A., 1923, i, 1203).—The preparation of the second isomeride of iodo-*p*-hydroxybenzoic acid (2 : 4 : 1) is described. Treatment of the diazonium sulphate derived from 4-nitroanthranilic acid with potassium iodide yields 2-iodo-4-nitrobenzoic acid (cf. Willgerodt and Gartner, A., 1908, i, 877), which on reduction yields *2-iodo-4-aminobenzoic acid*, colourless needles, m. p. 188° (decomp.); *hydrochloride*, decomp. 210°; *sulphate*, white needles. The diazonium sulphate derived from this acid decomposes in aqueous solution, forming *2-iodo-4-hydroxybenzoic acid*, white, refractive needles, m. p. 215° (decomp.); *acetyl* derivative, m. p. 146°. J. W. B.

Phthalaldehydic Acid. L. SEEKLES (*Rec. trav. chim.*, 1924, **43**, 329—340).—Further details of the preparation of phthalaldehydic acid by the ozonisation of naphthalene are given (cf. A., 1923, i, 931). The normal phenylhydrazone of phthalaldehydic acid has not previously been described, as it readily loses water to form phenylphthalazone. It has now been obtained by the action of phenylhydrazine on the sodium salt of the acid. *Benzaldehyde-phenylhydrazone-o-carboxylic acid* forms a yellow precipitate, m. p. 100° (decomp.); the dark yellow *sodium* salt contains $4H_2O$, and the yellow *silver* salt turns brown in the light. Similar compounds were obtained using *p*-bromo- and *p*-nitro-phenylhydrazine. p-*Bromophenylphthalazone* forms fine, colourless needles, m. p. 169·5°; p-*nitrophenylphthalazone*, orange crystals, m. p. 259° (sintering from 228°). Hydrogen cyanide combines with the aldehydic group of phthalaldehydic acid in the normal manner, forming *o*-carboxymandelonitrile, from which *o*-carboxymandelic acid is obtained, by hydrolysis with hydrochloric acid, in the form of its lactone, phthalide-α-carboxylic acid. With acetic anhydride, phthalaldehydic acid forms a monoacetyl derivative, which must also have the phthalide structure, $C_6H_4<\begin{matrix}CH(OAc)\\CO\end{matrix}>O$. Its m. p. is 71°, not 60—63° as recorded elsewhere.

Comparison of the molecular refraction of phthalaldehydic acid in alcoholic solution with that of phthalide and phthalidecarboxylic acid shows that in this solvent phthalaldehydic acid has the phthalide structure, whilst in aqueous solution the aldehydic tautomeride is the more stable form. E. H. R.

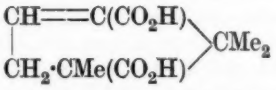
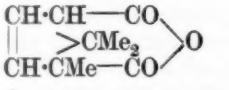
Benzylidenepyruvic Acid [Styrylglyoxylic Acid] and its Esters. I. The Action of Sunlight on Crystalline Methyl Styrylglyoxylate. M. REIMER (*J. Amer. Chem. Soc.*, 1924, **46**, 783—790).—Erlenmeyer's procedure for preparing styrylglyoxylic acid by condensing pyruvic acid and benzaldehyde in presence of sodium hydroxide (A., 1903, i, 698) has been improved and the yield increased to 80% of the theoretical. The *ethyl* ester is a yellow oil, b. p. 169—171°/7 mm.; the *methyl* ester forms long, yellow needles, m. p. 73—74°. After 1 month's exposure to sunlight, the methyl ester changes into a dimeric form, $(C_{11}H_{10}O_3)_2$, shown to be *methyl* 2 : 4-*diphenyl*cyclo*butane*-1 : 3-*diglyoxylate*, $\begin{matrix}Ph\cdot CH—CH\cdot CO\cdot CO_2Me\\ |\quad\quad |\\ CO_2Me\cdot CO\cdot CH—CHPh\end{matrix}$, colourless crystals, m. p. 154°, which by hydrolysis yields the corresponding *acid*, m. p. about 187° (in some cases after melting at 110—116°, with evolution of gas, and again solidifying). When re-methylated with methyl alcohol, the acid gives an *ester*, $(C_{11}H_{10}O_3)_2$, m. p. 155°, not identical with the ester having m. p. 154°, but readily obtained from it by the action of hydrogen chloride in methyl alcohol. Oxidation of the above acid gives α-truxillic acid, which proves its constitution.

When methyl styrylglyoxylate dissolved in benzene is exposed to sunlight, a third isomeric *methyl* ester is obtained as colourless crystals, m. p. 117°. Hydrolysis of this ester gives an acid, m. p.

180°, which when esterified with methyl alcohol again forms the ester from which it had been produced. The free acid, when oxidised, is converted into δ-truxinic acid and is therefore concluded to be 3 : 4-*diphenyl*cyclo*butane*-1 : 2-*diglyoxylic acid*. C. J. S.

Saponins and Related Compounds. X. Urson. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1924, **43**, 367—379).—The m. p. of chemically pure urson is 279—280° (cf. Dodge, A., 1919, i, 91). The generally accepted composition of urson, $C_{30}H_{48}O_3$, is incorrect, the correct formula being $C_{31}H_{50}O_3$. This formula explains the decomposition of urson, when distilled with zinc dust in a current of hydrogen, into sesquiterpenes, carbon dioxide, and water: $C_{31}H_{50}O_3 \longrightarrow 2C_{15}H_{24}+CO_2+H_2O$. The sesquiterpenes when heated with sulphur (Ruzicka's method) give an oil of which a *picrate*, m. p. 115—116°, was obtained; this is probably a picrate of a hydrocarbon of the naphthalene series, but is not identical with cadalene picrate. Urson contains one hydroxyl and one carboxyl group. *Acetylurson*, m. p. 200—201°, obtained by the action of acetic anhydride on urson, is deacetylated by boiling alcohol, consequently the " acetylurson " obtained by Gintl (A., 1893, i, 601) was urson itself. Dodge (*loc. cit.*) described a diacetylurson, and supposed urson to be a hydroxy-lactone, but his product probably contained occluded acetic anhydride. Methylation of urson takes place in the carboxyl group, giving methyl urson, which forms a *hydrate* containing $1H_2O$, m. p. 120°; anhydrous methyl urson has m. p. 165°, not 148° (cf. Nooyen, *Diss.*, Leyden, 1920). *Methyl acetylurson*, long, glistening needles, m. p. 245°, is more stable than acetylurson. The influence of the free carboxyl group on a neighbouring hydroxyl group has been also observed in the case of saponins (*e.g.*, hederagenin, A., 1922, i, 160). E. H. R.

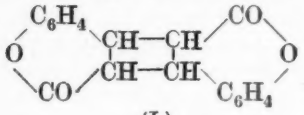
Steric Hindrance in Bridged Rings (Bredt's Rule) and the *meso-trans*-Position in Condensed *cyclo*Hexane Ring Systems. J. BREDT, H. THOUET, and J. SCHMITZ (*Annalen*, 1924, **437**, 1—13).—The author adduces facts in agreement with his rule (cf. A., 1902, i, 374; 1913, i, 281; 1917, i, 655) that double bonds cannot exist in conjunction with the " bridge-heads " in bridged *cyclo*hexane structures. He now shows that a bridged (7-membered) ring of this kind cannot be formed. Thus, such a dicarboxylic acid as dehydrocamphoric acid (I) does not yield a simple anhydride, but gives ultimately the anhydride of *iso*dehydrocamphoric acid (II):

(I.)  (II.) 

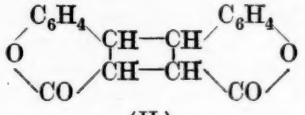
Silver dehydrocamphorate and dehydrocamphoryl chloride heated together produce an amorphous *dianhydride*, sintering at 120°, but having no definite m. p. Dehydrocamphoric acid heated with acetyl chloride yields the acid chloride and a *mixed anhydride*, and the latter compound is also formed when the acid is heated with acetic anhydride. It forms a syrupy mass; when heated further,

it decomposes, giving a *poly-anhydride* of dehydrocamphoric acid, a vitreous substance, which when distilled in a vacuum yields iso-*dehydrocamphoric anhydride*, stout crystals, m. p. 184°. The conclusion that dehydrocamphoric acid can yield no simple anhydride is supported by steric considerations, and for these reasons the author concludes that the anhydrides obtained by Perkin (T., 1894, **65**, 572, 890) are likewise polymeric compounds. W. A. S.

Biscoumaric Acids. A. W. K. de Jong (*Rec. trav. chim.*, 1924, **43**, 316—322).—The author suggests that the biscoumarins have structures similar to those of the truxillic and truxinic acids (A., 1923, i, 574). There are thus four possible isomerides, two corresponding with the plane formula (I) and two with (II):



(I.)

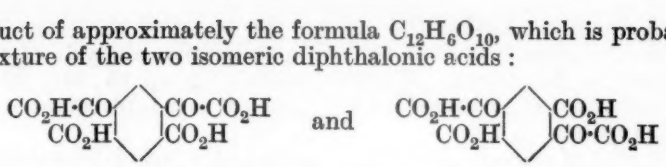


(II.)

The biscoumaric acid of Ström (A., 1904, i, 505) is formed by a method analogous to the formation of α-truxillic acid from α-cinnamic acid. It should therefore be called α-biscoumaric acid, and the biscoumarin derived from it is α-biscoumarin, m. p. 318° (decomp.). This should have formula I. It forms a *dimethyl ether*, colourless needles, m. p. 133°, which when hydrolysed gives α-biscoumaric acid dimethyl ether, m. p. 261—262°, which appears to be identical with the product obtained by Bertram and Kürsten by the action of light on coumaric acid methyl ether. When the dimethyl ether is heated with acetic anhydride, it forms *γ-biscoumaric acid dimethyl ether anhydride*, m. p. 186—187°, which when hydrolysed gives *γ-biscoumaric acid dimethyl ether*, brilliant needles, m. p. 234°. Another acid, *ε-biscoumaric acid*, m. p. 262°, was obtained by the action of fused potassium hydroxide on α-biscoumaric acid. The biscoumarin obtained by Ciamician and Silber (A., 1914, ii, 234) and called by them dihydrocoumarin, by the action of light on coumarin, is now called ζ-biscoumarin; m. p. 262°. This corresponds with formula II, and it is proposed to call the corresponding acids *biscoumarinic acids*, to correspond with the truxinic acids. *ζ-Biscoumarinic acid* is a dibasic acid, m. p. 245°, forming fine needles which soon grow into larger crystals. *Dimethyl ζ-biscoumarinate dimethyl ether* forms yellow crystals, m. p. 112—113°; *ζ-biscoumarinic acid dimethyl ether*, m. p. 134°. By heating with fused potassium hydroxide ζ-biscoumarinic acid is converted into *δ-biscoumarinic acid*, m. p. 157°. The hydrodicoumarin obtained by Dyson (*Chem. Soc. Trans.*, 1887, **51**, 66), by reducing dicoumarin with sodium amalgam, is not identical with ζ-biscoumarin, as supposed by Ciamician and Silber. By hydrolysis, it gives a monobasic acid. E. H. R.

Preparation of Pyromellitic Acid. J. von Braun and G. Lemke (*Ber.*, 1924, **57**, [*B*], 681—682).—The oxidation of octahydroanthracene with alkaline permanganate yields an acidic

product of approximately the formula $C_{12}H_6O_{10}$, which is probably a mixture of the two isomeric diphthalonic acids :



These could not, however, be separated. Further oxidation with acid permanganate gave a nearly quantitative yield of pyromellitic acid. From 30 g. of octahydroanthracene 41 g. of practically pure pyromellitic acid were obtained. F. A. M.

Action of Aluminium Alkoxides on Mixtures of Aldehydes. N. A. ORLOFF (*Bull. Soc. chim.*, 1924, [iv], **35**, 360—363; cf. A., 1907, i, 282).—The action of aluminium ethoxide on three mixtures of aldehydes has been studied. Benzaldehyde and *iso*butyraldehyde gave a product from which three fractions were obtained, the first consisting of *iso*butyl *iso*butyrate, the second of *iso*butyl benzoate (19·3%) and benzyl *iso*butyrate (80·7%), and the third of pure benzyl benzoate. From a mixture of *iso*butyraldehyde and acetaldehyde, in addition to *iso*butyl *iso*butyrate, ethyl acetate, and aldolic products, a mixture, b. p. 110—117·5°, was obtained consisting of *iso*butyl acetate (75%) and ethyl *iso*butyrate (25%). Benzaldehyde and acetaldehyde gave, besides ethyl acetate, benzyl benzoate, and unchanged benzaldehyde, a mixture of benzyl acetate (96·2%) and ethyl benzoate (3·8%). The author concludes that of the two possible mixed esters, that one will be formed in larger amount in which the aldehyde of higher molecular weight yields the alcoholic component. R. B.

Catalytic Hydration of Schiff's Bases. A. MAIHLE (*Bull. Soc. chim.*, 1924, [iv], **35**, 379—382; cf. A., 1919, i, 395; 1920, i, 380).—Schiff's bases are easily hydrolysed when vaporised in a current of steam and passed over catalysts such as thoria and alumina heated at 400°. In this way, benzylideneaniline, for example, yields benzaldehyde and aniline. In the presence of vapours of methyl or ethyl alcohol the amine is immediately alkylated, the product of the reaction being the corresponding dialkylamine, but in the presence of higher alcohols such as propyl alcohol, alkylation does not take place. R. B.

Thermochemical Researches on Stereoisomeric Aldoximes. W. SWIENTOSLAWSKI and M. POPOFF (*Bull. Soc. chim.*, 1924, [iv], **35**, 137—144).—Measurement of the heat evolved when sodium hydroxide or hydrochloric acid reacts with a stereoisomeric aldoxime (benzaldoxime, *m*-nitrobenzaldoxime) shows that the :N·OH group is more strongly acidic in the α-(*anti*)-aldoximes than in the β-(*syn*-)-aldoximes. The heat of solution in water is always negative, the β-isomeride having the higher absolute value.

Dry hydrogen chloride converts concentrated ethereal solutions of α-aldoxime into the β-stereoisomeride, but not always quantitatively. When a mixture of the two forms results, the α-aldoxime

is in greater proportion the greater the speed of the conversion. A thermochemical method for the quantitative analysis of these mixtures is developed. Mixtures containing up to 40% of the hydrochloride of α-benzaldoxime and of α-*m*-nitrobenzaldoxime were prepared.

The heat of conversion in ether solution of α- into β-benzaldoxime is −0·98 Cal.; that for α- into β-*m*-nitrobenzaldoxime is −1·18 Cal. The heats of transformation in the free state are +2·64 Cal. ($\alpha_{liq.}$ to β_{solid}) and −1·25 Cal. (α_{solid} to β_{solid}), respectively. E. E. T.

Derivatives of *p*-Nitrobenzaldehyde. II. C. G. KING and A. LOWY (*J. Amer. Chem. Soc.*, 1924, **46**, 757—762; cf. A., 1921, i, 337).—The following new *p*-nitrobenzylidene compounds have been prepared: p-*nitrobenzylidene*-o-*bromoaniline*, m. p. 106°; .m-*bromoaniline*, m. p. 102°; -2 : 6-*dibromoaniline*, m. p. 137°; -2 : 4 : 6-*tribromoaniline*, m. p. 142·5°; -3-*bromo*-4-*toluidine*, m. p. 112°; -p-*xylidine*, m. p. 100°; -o-*nitroaniline*, m. p. 169°. All form yellow needles except the last, which forms small plates.

p-Nitrobenzaldehyde condenses with 2 mols. of phenol by Danckworth's method, giving *p*-nitro-*p'p''*-dihydroxytriphenylmethane, which forms a 3' : 5' : 3'' : 5''-*tetrabromo* derivative, $NO_2 \cdot C_6H_4 \cdot CH:(C_6H_2Br_2 \cdot OH)_2$, small, yellow plates, m. p. 215°; *diacetyl* derivative, m. p. 168°.

The condensation product from resorcinol and *p*-nitrobenzaldehyde gave, on bromination, a *dibromo*-p-*nitrotetrahydroxytriphenylmethane*, $NO_2 \cdot C_6H_4 \cdot CH:[C_6H_2(OH)_2Br]_2$, a yellow, amorphous powder which turns red at 170° and chars above 200°. From *o*-nitrophenol and the nitro-aldehyde was obtained 4 : 3' : 3''-*trinitro*-4' : 4''-*dihydroxytriphenylmethane*, $NO_2 \cdot C_6H_4 \cdot CH:[C_6H_3(OH)NO_2]_2$, an orange, amorphous powder, m. p. 177°. The condensation product obtained from thymol and *p*-nitrobenzaldehyde was brominated and gave a *dibromo* derivative, $NO_2 \cdot C_6H_4 \cdot CH:[C_6HMePrBrOH]_2$, light orange crystals, m. p. 115°; *dibenzoyl* derivative, a pale yellow, amorphous powder, m. p. 82°. C. J. S.

Electrolytic Preparation of Salicylaldehyde from Salicylic Acid. K. S. TESH and A. LOWY (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 325—333).—Sodium salicylate is reduced electrolytically in the usual type of diaphragm cell with a mercury cathode, sodium sulphate being used as anolyte and a mixture of boric acid and sodium sulphate as catholyte. A current density of 6 amp. per sq. dm. is employed, and the temperature maintained at 15—18°; less aldehyde and more resinous matter is obtained at higher temperatures. The salicylaldehyde produced is fixed as soon as formed by progressive addition of sodium hydrogen sulphite, and is recovered by acid hydrolysis and distillation with steam. The best yield obtained is 55% of the theoretical. W. T. K. B.

Thermochemical Researches on Ketoximes. Non-stereoisomeric Ketoximes. A. DORABIALSKA (*Bull. Soc. chim.*, 1924, [iv], **35**, 145—152).—A thermochemical investigation of dimethyl, diphenyl, and phenyl methyl ketoximes (cf. Swientoslawski and Popoff, p. 645). According to theory two stereoisomeric phenyl

methyl ketoximes should exist, but only one could be obtained, treatment of ether or toluene solutions of the oxime with hydrogen chloride failing to cause any conversion. The heats of formation of the hydrochlorides of the oximes in ether solution differ but little from those of the aldoximes; they diminish with increasing acidity. Phenyl methyl ketoxime is more acidic than its constitution indicates. This is probably due to the ketoxime having the α-structure, since α-aldoximes are more acidic than the β-forms. The heat of solution of the hydrochlorides in 10% sodium hydroxide decreases as the acidity of the ketoxime increases. The heat is made up of four portions, viz., heat of solution of the hydrochloride in water (which is negative and less than that of the aldoximes), heat of decomposition (negative) of the hydrochloride into hydrochloric acid and oxime, heat of reaction of the oxime with sodium hydroxide, and heat of neutralisation of hydrochloric acid and sodium hydroxide. The parallel increase of the first two of these quantities is the cause of the decrease of the total heat with increasing acidity. E. E. T.

Ethyl Mercaptol of Phenyl Ethyl Ketone; a New Disulphone. A. SCHMIDT (*Bul. Soc. Chim. România*, 1924, **6**, 34—36).—On passing a stream of hydrogen chloride into a mixture of phenyl ethyl ketone (1 part) and ethyl mercaptan (2 parts) together with a small amount of anhydrous zinc chloride, the *ethyl mercaptol* of *phenyl ethyl ketone*, $CEtPh(SEt)_2$, a colourless oil of disagreeable odour, is formed. On oxidation with potassium permanganate in presence of dilute sulphuric acid, the corresponding *disulphone* is obtained in small yield as colourless, monoclinic plates, m. p. 113·5°. A. E. C.

Two Oximes of α-Ketotetrahydronaphthalene. H. INOUE (*J. Chem. Ind. Japan*, 1923, **26**, 1335—1338; cf. *Chem. Soc. Trans.*, 1899, **75**, 150).—The oxime of α-ketotetrahydronaphthalene, obtained by catalytic reduction of α-naphthol, is separated by steam distillation into a more volatile isomeride, A, colourless needles, m. p. 88—89°, and a less volatile, B, large, colourless prisms, m. p. 102—103°. By the Beckmann rearrangement, A gives B and B gives a nitrile-like liquid and another isomeric compound, C, colourless needles or prisms, m. p. 134—136°. A and B are probably stereoisomeric forms of the ketoxime. K. K.

Influence of Constitution on the Rotatory Power of Optically Active Substances. XVI. Acetylene Derivatives, Ketones, Carbylamines. H. RUPE (*Annalen*, 1924, **436**, 184—204; cf. A., 1909, i, 927).—A comparison has been made between the rotatory powers of compounds containing acetylenic linkings and the corresponding ethylenic and saturated compounds. Phenylacetylenylborneol, its dihydro- and tetrahydro-derivatives all exhibit normal rotation dispersion, and the ethylenic compound shows the greatest specific rotatory power. 1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl phenylacetylenyl ketone exhibits a large anomalous rotation-dispersion, whilst its dihydro and tetrahydro derivatives and also

an isomeric ethylenic compound obtained by the condensation of 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl methyl ketone with benzaldehyde (Rupe and Kloppenburg, A., 1919, i, 539) are nearly normal. Amylcarbylamine, hexonitrile, hexylamine, and benzylidenehexylamine all exhibit anomalous rotation-dispersion, which is total in the case of the first substance. 3-Methyl*cyclo*hexylcarbylamine and 3-methyl*cyclo*hexylamine show very similar dispersions and it is doubtful whether these are normal or not. α-Camphorcarbimide exhibits an enormous specific rotation in comparison with the other members of the series.

Phenylacetylenylborneol, $C_8H_{14}<\begin{matrix}CH_2\\ C(OH)\cdot C{:}CPh\end{matrix}$, from magnesium phenylacetylenyl bromide and camphor, has b. p. 190°/13 mm. or 125—126°/0·1 mm., m. p. 44—45°, $[\alpha]_D^{20}$ −27·37° in 10% benzene solution.

Styrylborneol, $C_8H_{14}<\begin{matrix}CH_2\\ C(OH)\cdot CH{:}CHPh\end{matrix}$, was obtained from the preceding compound by regulated reduction with hydrogen and a nickel catalyst in a mixture of aqueous alcohol and ethyl acetate. It forms a colourless, viscous oil, b. p. 183—186°/11 mm., 106—107°/0·1 mm.; $[\alpha]_D$ −107·7° in 10% benzene solution.

β-*Phenylethylborneol*, $C_8H_{14}<\begin{matrix}CH_2\\ C(OH)\cdot CH_2\cdot CH_2Ph\end{matrix}$, was obtained from the preceding compound by further reduction under identical conditions. It is a colourless, limpid oil, b. p. 176—179°/14 mm., 138—140°/0·5 mm.; $[\alpha]_D$ −25·45° in 10% benzene solution. By boiling for 12 hours with formic acid, it is dehydrated, and β-*phenylethylbornylene*, a limpid oil, b. p. 165—168°/12 mm., is formed.

Phenylacetylenylborneol, on boiling with formic acid, undergoes rearrangement to a *ketone* probably having the formula

$$C_8H_{14}<\begin{matrix}CH_2\\ C{:}CH\cdot COPh\end{matrix}$$

a yellowish-brown oil, b. p. 193—196°/12 mm., $[\alpha]_D$ −39·97° in 10% benzene solution; *semicarbazone*, white prisms, m. p. 155—156°; *phenylhydrazone*, yellow needles, m. p. 120—121°. By catalytic reduction, the ketone gives *phenyl camphanylmethyl ketone*,

$$C_8H_{14}<\begin{matrix}CH_2\\ CH\cdot CH_2\cdot COPh,\end{matrix}$$

white plates, m. p. 75—76°; $[\alpha]_D$ −16·66° in 10% benzene solution; *phenylhydrazone*, yellow needles, m. p. 110—111°; *semicarbazone*, m. p. 179—181°. 1 : 2 : 2 : 3-*Tetramethylcyclopentyl phenylacetylenyl ketone*, $C_8H_{14}Me\cdot CO\cdot C{:}CPh$, was synthesised from magnesium phenylacetylenyl bromide and campholic chloride, and formed needles, m. p. 53—54°; $[\alpha]_D$ +45·38° in 10% benzene. It was also obtained from sodium phenylacetylene and campholic chloride. The *phenylhydrazone* forms white needles, m. p. 137—138°, the *hydrazone*, needles, m. p. 123—124°. On warming with methyl-alcoholic potash, the ketone gave a viscous, yellow oil, b. p. 215—217°/13 mm., apparently an additive compound with 1 mol. of methyl alcohol. This methoxy compound gave a *phenyl-*

hydrazone, m. p. 144—145°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentyl styryl ketone*, from the acetylenic compound by reduction as before, is a pale yellow, somewhat viscous oil, b. p. 192—194°/12 mm., $[\alpha]_D$ +45·31° in benzene.

Its isomeride (cf. *supra*) has $[\alpha]_D$ +54·24° in 10% benzene solution. 1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl β-phenylethyl ketone may be obtained by the reduction of the acetylenic ketone (b. p. 178—181°/12 mm.; $[\alpha]_D$ +40·51° in 10% benzene solution) or of Rupe and Klottenburg's ketone (b. p. 188—189°/13 mm.; $[\alpha]_D$ +48·24° in 10% benzene solution), as well as by the method of Rupe and Jäggi (A., 1922, i, 840); (b. p. 178—181°/10 mm. and $[\alpha]_D$ +38·84° in 10% benzene solution).

Active amylcarbylamine has b. p. 137—138°/745 mm.; $[\alpha]_D$ +0·35° in benzene solution. Hexonitrile, hexylamine, and benzylidenehexylamine have $[\alpha]_D$ +0·76°, 0·86°, 1·41°, respectively. *Methyl*cyclo*hexylamine*, from the oxime of 3-methyl*cyclo*hexanone, has $[\alpha]_D$ −2·09°. By the action of chloroform and potassium hydroxide, 3-*methyl*cyclo*hexylcarbylamine* was obtained as an oil, b. p. 67—69°/10 mm.; $[\alpha]_D$ −0·77°. *Benzylidenehexylamine* is a colourless liquid, b. p. 130—132°/13 mm. A. E. C.

Equilibrium between Benzaldehyde and Benzoin. A. Lachman (*J. Amer. Chem. Soc.*, 1924, **46**, 708—723).—The condensation of 2 mols. of benzaldehyde to give 1 mol. of benzoin requires the combined action of hydroxyl and cyano ions. These catalysts also reverse the condensation, but at the same time they convert benzoin into benzyl benzoate and benzoic acid, this step not being reversible. When benzoin is heated at 300°, it is partly converted into benzaldehyde; under the same conditions, benzaldehyde yields no benzoin, but forms benzyl benzoate, benzoic acid, toluene, and dibenzyl ether. The benzoin and Cannizzaro condensations can be accounted for by two assumptions. Benzaldehyde combines with M·OH(or ·OR) to form the compound CHPh(OM)(OH) (A), in which ·OH is the more labile group; and with hydrogen cyanide to form CHPh(CN)(OH) (B), in which H is more labile. A reacts with benzaldehyde by transfer of hydroxyl to yield benzyl benzoate; it reacts with B according to the equation CHPh(CN)(OH) + CHPh(OH)(OK) = CPh(CN)(OK)·CH(OH)Ph + H_2O; if both benzaldehyde and B are present, it reacts with both; if A is absent, as in acidified solutions, benzoin fails to form. The unique function of the cyano ion as the only catalyst which will convert benzaldehyde into benzoin also becomes clearer. Benzaldehyde forms additive products of the general type CHPh(OH)(X) with sodium hydrogen sulphite, hydrogen chloride, and hydrogen cyanide, but of these the last is the only one capable of existing under conditions necessary for the presence of A, *i.e.*, alkaline solution. A method is described for preparing benzoin without the use of alcohol. C. J. S.

Optically Active β-Phthalimino-β-phenylpropiophenones. A. McKenzie and T. M. A. Tudhope (*J. Chem. Soc.*, **1924**, **125**, 923—930; cf. *ibid.*, 1921, **119**, 69).—In the preparation of *r*-β-amino-

β-phenylpropionic acid from hydroxylamine and cinnamic acid (cf. A., 1905, i, 577), besides acetophenoneoxime, 3-phenyl*iso*oxazolone, m. p. 149—151°, is produced (cf. A., 1906, i, 955; 1912, i, 453). *r*-β-Phthalimino-β-phenylpropionic acid was resolved into its optically active components with cinchonine in rectified spirit. From the more sparingly soluble cinchonine salt was separated d-β-*phthalimino*-β-*phenylpropionic acid*,

$$C_6H_4{:}C_2O_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

glassy rosettes, m. p. 150—151°, having $[\alpha]_D$ −5·5° in ethyl acetate, and −2·2° in ethyl alcohol. The same active acid was obtained by the resolution of *r*-β-amino-β-phenylpropionic acid (cf. A., 1910, i, 622) and heating the *d*-amino-acid with phthalic anhydride. In spite of its lævorotation in ethyl acetate, this acid is accordingly designated as *d*-β-phthalimino-β-phenylpropionic acid, taking *d*-β-amino-β-phenylpropionic acid as the reference compound. In methyl alcohol, the phthalimino acid is slightly dextrorotatory. Thionyl chloride converts the *d*-phthalimino acid into its acid chloride from which, by the Friedel-Crafts reaction, is obtained d-β-*phthalimino*-β-*phenylpropiophenone*,

$$C_6H_4{:}C_2O_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}COPh,$$

m. p. 116—117°, $[\alpha]_D^{15}$ −127·1° in benzene and $[\alpha]_D^{13}$ −96·2° in acetone. l-β-*Phthalimino*-β-*phenylpropiophenone* was similarly obtained from the *l*-phthalimino acid. Hydrolysis of the lævorotatory *d*-ketone with alcoholic sodium hydroxide yields d-β-*benzoyl*-α-*phenylethylphthalamic acid*, $COPh{\cdot}CH_2{\cdot}CHPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, feathery crystals, m. p. 147—147·5°, $[\alpha]_D^{16·5}$ +38·8° in ethyl alcohol, which on hydrolysis with a mixture of concentrated hydrochloric acid and glacial acetic acid yields phthalic acid and the lævorotatory *d*-β-phthalimino-β-phenylpropiophenone, dehydration as well as hydration of the phthalamic acid taking place. R. B.

Migration of Groups in Derivatives of Benzoin and Desylamine. A. McKenzie and R. Roger (*J. Chem. Soc.*, 1924, **125**, 844—854; cf. A., 1923, i, 213, 333, 788).—The dehydration of methylhydrobenzoin with concentrated sulphuric acid yields a methyldeoxybenzoin, m. p. 50—52° (cf. Tiffeneau and Orékhov, A., 1920, i, 672; 1921, i, 565; Lévy, A., 1921, i, 860), from which two semicarbazones were obtained, m. p. 213—215° (cf. A., 1920, i, 672) and 159—160°. The methyldeoxybenzoin thus appears to exist in two forms, one melting at 50—52° (cf. A., 1888, 703) and the other at 58—59°. Both forms are converted into ααβ-triphenyl-α-propanol, m. p. 88—89°, with magnesium phenyl bromide. A small amount of *as*-diphenylacetone is also formed in the dehydration of the glycol as a result of slight semipinacolin transformation. The dehydration of αα-diphenylpropane-αβ-diol with either dilute or concentrated sulphuric acid (cf. A., 1906, i, 724) yields *as*-diphenylacetone: $OH{\cdot}CPh_2{\cdot}CHMe{\cdot}OH \longrightarrow CHPh_2{\cdot}COMe$, vinyl dehydration being the only change which occurs. The ketone has m. p. 58·5—59·5° and its semicarbazone m. p. 169—170° (cf. A., 1906, i, 581). β-Hydroxy-αβ-diphenylpropylamine on treatment with sodium nitrite in acetic acid solution undergoes semi-

pinacolinic deamination and yields *as*-diphenylacetone, m. p. 45—47° when freshly prepared, rising to 58—59° after 4 weeks. The transformation: $OH{\cdot}CPhMe{\cdot}CHPh{\cdot}NH_2 \longrightarrow COMe{\cdot}CHPh_2$, is in marked contrast to the vinyl dehydration of methylhydrobenzoin: $OH{\cdot}CPhMe{\cdot}CHPh(OH) \longrightarrow CHPhMe{\cdot}COPh$. Other examples of the action of nitrous acid on amino-alcohols cited by McKenzie and Richardson (T., 1923, **123**, 79) are interpreted on similar lines. In the light of this work, the product, $C_{21}H_{18}O$, m. p. 121·5—122°, obtained by McKenzie and Richardson by the action of nitrous acid on γ-hydroxy-αγγ-triphenyl*iso*propylamine,

$$CH_2Ph{\cdot}CH(NH_2){\cdot}CPh_2{\cdot}OH,$$

is benzyldeoxybenzoin (cf. Meyer and Oelkers, A., 1888, 703), semipinacolinic deamination taking place. A further example of this change is the conversion by nitrous acid of β-hydroxy-αββ-triphenylethylamine into phenyldeoxybenzoin.

The dehydration of αβ-diphenyl-β(α-naphthyl)-ethane-αβ-diol, m. p. 204—205° (cf. A., 1904, i, 742), with dilute sulphuric acid yields a compound, $C_{24}H_{18}O$, m. p. 180—181°, probably the ethylenic oxide, $O<\begin{matrix}CHPh\\ |\\ CPh{\cdot}C_{10}H_7\end{matrix}$. Concentrated sulphuric acid yields an isomeride, m. p. 108—109°, identical with the product obtained by the action of nitrous acid on β-hydroxy-αβ-diphenyl-β-naphthylethylamine (T., 1923, **123**, 79). R. B.

Stereochemical Investigations in the Phenyl Styryl Ketone Series. Certain Derivatives of Dibenzoylmethane and of Phenyl Styryl Ketone. C. Dufraisse and A. Gillet (*Compt. rend.*, 1924, **178**, 948—950).—The phenyl β-alkoxystyryl ketones, $COPh{\cdot}CH{:}CPh{\cdot}OR$ (A., 1923, i, 113) combine with bromine without forming any appreciable proportion of hydrogen bromide, but the dibromo compounds obtained, $COPh{\cdot}CHBr{\cdot}CBr(Ph){\cdot}OR$, are extremely sensitive to the action of moisture and undergo immediate transformation into bromodibenzoylmethane, $COPh{\cdot}CHBr{\cdot}COPh$. When special precautions are taken, it is, however, possible to replace by a second alkoxy group the bromine atom of the $\cdot CBr(Ph){\cdot}OR$ group. In this way, good yields of the following monoacetals of bromodibenzoylmethane were obtained: *phenyl α-bromo-ββ-dimethoxy-β-phenylethyl ketone*, $CHBrBz{\cdot}CPh(OMe)_2$, m. p. 91°; corresponding *diethoxy* compound, $CHBrBz{\cdot}CPh(OEt)_2$, m. p. 72°; *dipropoxy* compound, $CHBrBz{\cdot}CPh(OPr)_2$, m. p. 84°. Of the two possible racemic compounds represented by the formula, $CHBrBz{\cdot}CPh(OMe){\cdot}OEt$, only one, m. p. 90°, has yet been obtained.

These acetals are white compounds and are particularly sensitive towards acids, which convert them immediately into bromodibenzoylmethane. When heated, they lose 1 mol. of an alcohol giving pale yellow phenyl α-bromo-β-alkoxystyryl ketones, of which the following have been prepared: *phenyl α-bromo-β-methoxystyryl ketone*, $CBrBz{:}CPh{\cdot}OMe$, m. p. 72° (stable form); corresponding β-*ethoxy* compound, $CBrBz{:}CPh{\cdot}OEt$, m. p. 76° (stable form); and β-*propoxy* compound, $CBrBz{:}CPh{\cdot}OPr$, m. p. 49°.

These undergo hydrolysis when heated with a dilute acid, bromodibenzoylmethane being formed. The action on them of an alkali alkoxide results in the fixation at the double linking of an alcohol molecule, the resulting monoacetals being either symmetrical or unsymmetrical.

The phenyl α-bromo-β-alkyloxystyryl ketones are prone to exist in several forms, each having characteristic crystallographic constants, melting point, and solubility. Thus, the methoxy compound exhibits two forms, m. p. 64° and 72°, and the ethoxy compound, three forms, m. p. 65°, 73°, and 76°. The form with the highest melting point is the most stable, and when it has once made its appearance in a laboratory, the preparation there of the other form or forms is impossible unless the precautions employed in obtaining pure cultures of bacteria are taken.

The unstable form of phenyl α-bromo-β-methoxystyryl ketone, m. p. 64°, is isomorphous with the stable form of phenyl αβ-dibromostyryl ketone, m. p. 80°, and with the unstable form, m. p. 71°, of one of the di-iodo derivatives of phenyl styryl ketone. T. H. P.

Stereoisomeric Semicarbazones. F. J. Wilson and R. M. Macaulay (*J. Chem. Soc.*, **1924**, **125**, 841—844; cf. *ibid.*, 1912, **101**, 1482; 1913, **103**, 377, 1504).—By exposure to ultra-violet light dypnone semicarbazone, $CPhMe{:}CH{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 151°, has been converted into a second of the four stereoisomerides required by theory. The new semicarbazone, m. p. 175—176°, is obtained in a yield of 33% of theory, and partial reconversion is effected on further exposure. Similarly, the δ-phenylsemicarbazone of mesityl oxide, m. p. 134°, yields about 33% of a more soluble *stereoisomeride*, m. p. 99—101°, reconversion being accomplished by heating in alcoholic solution. The semicarbazone of phenyl β-phenylstyryl ketone, m. p. 171—172° (cf. A., 1916, i, 821) yields, in the same way, the second stereoisomeric carbazone required by theory, a pale yellow, microcrystalline powder, m. p. 204—205°, partial transformation of either stereoisomeride taking place on exposure in alcoholic solution. Attempts to obtain a stereoisomeride of styryl *iso*butenyl ketone semicarbazone, $CMe_2{:}CH{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH{:}CHPh$, m. p. 168°, were unsuccessful. In the preparation of the semicarbazone, a small quantity of a substance, m. p. 221—222°, possibly the semicarbazide-semicarbazone,

$CMe_2(NH{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}C(:N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH{:}CHPh$,

was obtained. Attempts to obtain stereoisomerides of the semicarbazones of benzylacetone, benzylacetophenone, and styryl methyl ketone were also unsuccessful. R. B.

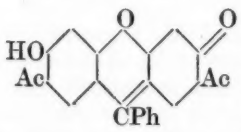
Indones. V. Conversion of 3-Phenyl-2-methylindone into Diphenyldimethyltruxones by the Action of Ultra-violet Rays. R. de Fazi (*Gazzetta*, 1924, **54**, 85—88; cf. A., 1920, i, 316; 1921, ii, 357).—It has been shown previously that, when treated with cold, concentrated sulphuric acid, ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate yields 3-phenyl-2-methylindone, whereas ethyl

β-hydroxy-ββ-diphenylpropionate gives 3-phenylindone and the two diphenyltruxones (A., 1915, i, 1063; 1916, i, 151; 1920, i, 316; 1921, ii, 357). Under the same conditions, 3-phenyl-2-methylindone yields no truxone, but may be recovered unchanged from the emerald-green solution formed.

The two *diphenyldimethyltruxones* (cf. A., 1920, i, 317) are, however, formed when a benzene solution of 3-phenyl-2-methylindone is subjected in a quartz tube to the influence of the ultraviolet light from a quartz mercury vapour lamp. The first *isomeride* forms pale, canary-yellow crystals, m. p. 259—260°; the second *isomeride* forms white crystals, m. p. 307—308°, appears to be phototropic, and, after repeated crystallisation from alcohol, yields 3-phenyl-2-methylindone when treated with concentrated sulphuric acid. T. H. P.

The Benzil Rearrangement. VI. A. Lachman (*J. Amer. Chem. Soc.*, 1924, **46**, 779—782; cf. A., 1923, i, 784, 785).—In the benzil rearrangement there are two opposing reactions: one, consisting of intramolecular oxidation and reduction, giving benzilic acid; and the other, a process of rupture, producing benzaldehyde and ethyl benzoate. The first reaction will not occur in the absence of water, but a much smaller quantity of water will suffice if ether is used as a part of the solvent, and if potassium hydroxide is employed in place of sodium hydroxide. As the proportion of water increases, less benzoic acid, but more benzilic acid, results. Schönberg and Keller (A., 1923, i, 928) ascribe the formation of benzoic acid during the benzil rearrangement to oxidation by atmospheric oxygen, but it is shown that such an action does not occur. C. J. S.

Condensation of Benzoic Acid and Substituted Benzoic Acids with Resacetophenone. G. C. Chakravarti (*J. Amer. Chem. Soc.*, 1924, **46**, 682—685).—A number of dyes belonging to the benzein series have been prepared by heating, in presence of anhydrous zinc chloride, 2 mols. of resacetophenone with rather more than 1 mol. of benzoic or a substituted benzoic acid. The dyes show strong fluorescence in alkaline solution and yield colourless acetyl derivatives. Benzoic acid condensed with resacetophenone gives *resacetophenonebenzein* (annexed formula), forming rose-red crystals, m. p. 141°; *acetyl* derivative, m. p. 125°. *Resacetophenone-p-hydroxybenzein*, $C_{23}H_{16}O_6,4H_2O$, from *p*-hydroxybenzoic acid, has m. p. 107—108°, and when kept for several weeks is transformed into a "homochromo-isomeride," m. p. 192°; *acetyl* derivative, m. p. 102°. Salicylic acid yields a *benzein*, m. p. 133—135° (*acetyl* derivative, m. p. 128°). The *benzeins* obtained from anisic acid, *m*-bromobenzoic acid, and gallic acid have m. p. 161°, 147°, and 126°, respectively. Similarly constituted products of high m. p. are obtained from *m*- and *p*-nitro- and *p*-chlorobenzoic acids. C. J. S.



Constitution of Biochemically Formed Hydroxyketopropylbenzene. C. NEUBERG (*Biochem. Z.*, 1924, **144**, 44—46).—A reply to Auwers and Jordan (this vol., i, 384). It is pointed out that the structure ascribed by these authors to the β-ketol is in agreement with the views of Neuberg and Ohle, and that the exact constitution of the product formed by the action of carboligase in the presence of benzaldehyde is of little importance to the biological aspect of the activity of the enzyme. J. P.

Functions of Chromophores. IX. The Quinone Chromophore. I. J. LIFSCHITZ, H. LOURIÉ, J. ZIMMERMANN, and G. A. TEN BOKKEL HUININK (*Rec. trav. chim.*, 1924, **43**, 269—282; cf. A., 1921, ii, 286, 287).—The absorption spectrum of *p*-benzoquinone in alcoholic solution consists of three bands with maxima at 2150 (A), 3400 (B), and 4400 (C). These bands may be assumed to correspond with the three groups of absorption bands of the vapour spectrum, and may therefore be attributed to different species of electrons or different groups of atoms. Substitution of the hydrogen atoms of *p*-benzoquinone by alkyl groups, as in toluquinone and *p*-xyloquinone, moves A without weakening it towards shorter wave-lengths, B and C in the opposite direction. Unsaturated hydrocarbon groups, as in anthraquinone, weaken A and strengthen B. Chlorine has a similar effect, but influences C irregularly. Chloranil owes its intense yellow colour to the broadening of B. Auxochromic groups having no residual valency, such as the ethoxy group, have a similar effect to chlorine, but intensified, whilst auxochromic groups having residual valency (·OH and ·NR_2) have such an extreme effect as to give the substance the character of a dyestuff. From the effect of chlorine on band A it is argued that this band is associated with the carbon atoms, since chlorine has the effect of weakening the conjugated system of the carbonyl groups and ethylenic linkings. This deduction is supported by the fact that A is strengthened and deepened in polynuclear quinones. Band B is attributed to the oxygen electrons, since the broadening of this band by alkyl groups and its shifting towards the red by halogens is similar to the effect of these radicals on the oxygen band of acetone. E. H. R.

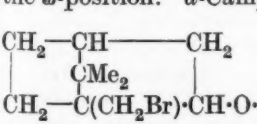
Quinhydrone Salts. S. GOLDSCHMIDT and F. CHRISTMANN (*Ber.*, 1924, **57**, [*B*], 711—715).—The sodium salt of *p*-benzoquinhydrone, $C_6H_4O_2+C_6H_4O_2Na_2$, was obtained practically pure by treating a mixture of quinone and quinol with sodium ethoxide in dry ethereal solution; it formed a deep blue precipitate sufficiently stable, when dry, to be weighed in air. The blue *sodium* salt of *o-benzoquinhydrone* was obtained in a similar manner, in complete absence of air or moisture. Both salts are at once decomposed by water to give greenish-yellow or brown solutions respectively. The *sodium* salt of *phenanthraquinhydrone* was obtained as a deep green precipitate by dissolving phenanthraquinol in alcohol or pyridine, adding 10% sodium hydroxide and 10% sodium chloride solution, and then blowing in oxygen. It is practically insoluble in water in absence of air, but dissolves in

pyridine to a deep green solution. The corresponding *barium* salt was also prepared. On treating a benzene solution of phenanthraquinol with lead dioxide, an emerald-green solution is obtained which is believed to contain a complex salt of the type ($x C_8H_{14}O_2 + y C_8H_{14}O_2Pb$). F. A. M.

Direct Amination of Anthraquinone. J. KNIATOWNA (*Bull. Soc. chim.*, 1924, [iv], **35**, 207—211).—According to a German patent (D.R.-P. 287756), the product obtained by heating anthraquinone with hydroxylamine sulphate in concentrated sulphuric acid, in presence of ferrous sulphate for 2 hours at 180—190°, is practically pure 1-aminoanthraquinone. This claim cannot be substantiated. Only a very small portion of the product dissolves in hydrochloric acid, and the residue, after repeated crystallisation, gives anthraquinone. From the mother-liquors of these crystallisations molecular compounds of anthraquinone and aminoanthraquinone are obtained which melt between 253° and 271°. The formation of such compounds may be the cause of the contradictory values given in the literature for the melting point of 1-aminoanthraquinone. E. E. T.

Anthraquinonylsemicarbazides. M. BATTEGAY and P. DASSIGNY (*Bull. Soc. chim.*, 1924, [iv], **35**, 211—213).—Dianthraquinonylsemicarbazides are prepared by boiling together nitrobenzene solutions of β-anthraquinonylcarbamyl chloride and α- or β-anthraquinonylhydrazine. *ββ′-Dianthraquinonyl-1:4-semicarbazide*, $\beta\text{-}C_{14}H_7O_2\cdot NH\cdot NH\cdot CO\cdot NH\cdot\beta\text{-}C_{14}H_7O_2$, is an orange substance which turns orange-yellow at 300°, sublimes, and leaves a residue melting above 330°. *αβ′-Dianthraquinonyl-1 : 4-semicarbazide* is a reddish brown substance which turns orange at 270—275° and melts at about 310°. Both these compounds dye cotton from a hyposulphite vat, but the dyeings are irregular owing to partial decomposition taking place in the bath. E. E. T.

Constitution of so-called β-Bromocamphor. P. LIPP and F. LAUSBERG (*Annalen*, 1924, **436**, 274—286).—Although Wedekind, Schenk, and Stüsser have shown (A., 1923, i, 346) that Reychler's camphorsulphonic acid is an ω-derivative, the formation of "β"-bromocamphor from camphorsulphonyl bromide (*Chem. Soc. Proc.*, 1901, **17**, 244, 245) affords no proof of the ω-constitution of the bromocamphor owing to the possibility of isomeric change. The authors have accordingly attempted the preparation of "β"-bromocamphor from compounds containing the bromine atom in the ω-position. *d*-Camphene was converted into ω-bromocamphene, which by digestion with trichloroacetic acid at 40° yields the well-crystallised *trichloroacetate* (annexed formula), which was obtained in two stereoisomeric forms, m. p. 80° and 101—102°. On hydrolysis, the expected ω-bromo-borneol or -*iso*borneol was not obtained but by reduction with sodium amalgam in alcoholic solution the ester yields the α-campholen-



aldehyde of Ciamician and Silber (A., 1910, i, 496), b. p. 93·5—96°/19 mm. (*semicarbazone*, m. p. 160—162°). The aldehyde is easily resinified by alkalis and a resinous *substance*, $(C_{10}H_{16}O)_n$, b. p. 165—175°/4 mm., was isolated as a by-product in the reduction.

On oxidation with nitric acid, *d*-ω-2-dibromocamphane gives an acid, $C_{10}H_{15}O_4Br$, m. p. 208—210°, an oily product containing nitrogen and halogen, which yields a yellow potassium salt, and a neutral substance, probably $C_8H_{13}Br<\begin{matrix}CH_2\\ |\\ CH_2\cdot NO_2\end{matrix}$. The acid is identical with the "β"-bromocamphoric acid obtained by the oxidation of "β"-bromocamphor, the identity being confirmed by a comparison of the anhydrides. The m. p. of ω-bromocamphoric anhydride is given as 149—150° (cf. P., 1901, **17**, 244). *dl*-ω-2-Dibromocamphane similarly gives *dl*-ω-bromocamphoric acid (decomp. 208—210°), and the corresponding anhydride, m. p. 149—149·5°. For comparison *dl*-ω-camphorsulphonic acid was prepared from synthetic camphor by Reychler's method (A., 1899, i, 445) and from this, by Armstrong and Lowry's procedure, the *dl*-ω-bromocamphor, m. p. 76—77°, was obtained. On oxidation with nitric acid, this yields *dl*-ω-bromocamphoric acid, m. p. 210—211°, and anhydride, m. p. 149—150°, identical with the products obtained from *dl*-ω-2-dibromocamphane, and the authors accordingly assign the ω-structure to "β"-bromocamphor. R. B.

Optically Active Sulphilimines. F. G. Mann and W. J. Pope (*J. Chem. Soc.*, 1924, **125**, 911—918).—Attempts have been made to prepare sodium *d*-α-bromocamphor-π-sulphonchloroamide and by condensation with methyl ethyl sulphide to obtain the corresponding sulphilimine, $C_{10}H_{14}OBr\cdot SO_2N{:}SMeEt$, which, owing to the trihedral disposition of the three valencies of the doubly-linked nitrogen atom, should exist in two enantiomorphous forms. *d*-Bromocamphor-π-sulphonamide, on treatment with sodium hypochlorite, gives d-*bromocamphor-π-sulphondichloroamide*,

$$C_{10}H_{14}OBr\cdot SO_2\cdot NCl_2,$$

white crystals, m. p. 123—125°, which slowly lose chlorine on standing. No sodium or potassium salt could be obtained, and by treatment with alcoholic potassium hydroxide (either with or without ethyl sulphide) the dichloroamide yielded unchanged α-bromocamphor-π-sulphonamide and d-α′-*chloro*-α-*bromocamphor-π-sulphonamide*, $C_{10}H_{13}OClBr\cdot SO_2\cdot NH_2$, colourless needles, darkening at 225°, m. p. 232° (decomp.) (cf. Lapworth, T., 1899, **75**, 558). For comparison, the d-α-*chloro*-α′-*bromocamphor-π-sulphonamide*, colourless needles, darkening at 224°, m. p. 232° (decomp.), was prepared by brominating ammonium *d*-α-chlorocamphor-π-sulphonate, treating the product with phosphorus pentachloride, yielding d-α-*chloro*-α′-*bromocamphor-π-sulphonyl chloride*, colourless crystals, m. p. 194—197° (effervescence), which with ammonia gives the sulphonamide. The two sulphonamides differ only in rotatory constants. d-α-*Bromocamphor-π-sulphonethylchloroamide*, $C_{10}H_{14}OBr\cdot SO_2\cdot NEtCl$, white crystals, m. p. 122—124° (efferv.), from *d*-α-bromocamphor-π-sulphonyl chloride and ethylamine is

more stable than the dichloroamide, and can be crystallised from alcohol.

Sodium ethyl sulphide condenses with *d*-chloromethylenecamphor, giving *ethylthiolmethylene*-d-*camphor*, $C_{10}H_{14}O{:}CH{\cdot}SEt$, pale green liquid, b. p. 169—171°/17 mm., $d_{4^\circ0}^{14^\circ3}$ 1·0362. *Ethylthiolmethylene*-l-*camphor*, obtained similarly, is a pale green liquid, b. p. 168—169°/16 mm., $d_{4^\circ0}^{15^\circ0}$ 1·0357. Both sulphides condense with hydrated "chloramine-*T*" in boiling alcohol to give d- and l-*camphorylidenemethylethylsulphine*-p-*toluenesulphonylimine*,

$$C_{10}H_{14}O{:}CH{\cdot}SEt{:}N{\cdot}SO_2{\cdot}C_7H_7,$$

white crystals, m. p. 172° (efferv.). The rotatory powers of these sulphilimines are less than those of the parent substances, and no indication was obtained of the expected stereoisomerism. Rotatory powers are given for all the above compounds. R. B.

The Beckmann Rearrangement. X. S. Komatsu (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 147—150).—The author cites various examples of the Beckmann change and of nitrile formation, and points out that the latter reaction may be due to direct elimination of water from the oxime or to dehydration after the Beckmann change. C. J. S.

The Beckmann Rearrangement. XI. Catalytic Action of Reduced Copper on *l*-Menthoneoxime. S. Komatsu and M. Kurata (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 151—156).—When *l*-menthoneoxime and pure hydrogen were passed over reduced copper at 200°, the product contained menthone, dimenthylamine, *l*-menthylamine, *d*-menthylamine, menthonitrile, decenoic acid and its amide, and a basic substance, probably 4-methyl-7-*iso*propyl-*cyclo*hexenimine, $Pr^{\beta}{\cdot}CH\langle^{NH{\cdot}CH{:}CH}_{CH_2---CH_2}\rangle CHMe$ (cf. Wallach, A., 1903, i, 104). The production of the last is regarded as evidence of the momentary formation of menthone*iso*oxime, which undergoes the Beckmann rearrangement by catalytic action of the reduced copper. The menthonitrile and decenoic acid are supposed to be formed respectively by catalytic dehydration and hydration of decenamide. C. J. S.

Camphor Oils. I. Reaction between Camphor-red Oil and Sulphuric Acid. K. Ono (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 99—105).—According to Sugiyama (Japanese Pat. 37119, 1920), terpin hydrate is obtained when camphor-red oil is treated with sulphuric acid. The author shows that this result is due to the action of the acid on the terpineol present in the oil (cf. Aschan, A., 1919, i, 336) and gives the conditions to be employed in order to obtain the optimum yield of terpin hydrate. [Cf. *B.*, 1924, 447.] T. H. P.

Origin of Terpenes and Crystalline Acids in Pine Resins. G. Dupont (*Compt. rend.*, 1924, **178**, 1560—1562).—The hypothesis that the terpenes and resin acids in conifers have a common origin in a material secreted by the resin cells is developed. The secreted material, which has the formula $C_{10}H_{16}O$ (Köhler, A., 1912, i, 638),

is converted by the action of a diastase into the terpene, $C_{10}H_{16}$, and the oxygen acting on two other molecules produces the resin acids, $3C_{10}H_{16}O=C_{10}H_{16}+C_{20}H_{30}O_2+H_2O$. This requires that the refined turpentine should contain 31% of the essential oil and 69% of resin acids, numbers which are in close agreement with the proportions actually found. The proportions of *d*- and *l*-pimaric acids and resin acids in the extract of the maritime pine, the fact that *d*-pimaric acid is found only in turpentines rich in nopinene, whilst the Aleppo pine, which yields only pinene, gives an extract containing alepic acid only, all support the hypothesis. J. W. B.

Eutectics of Camphene with other Terpenes. G. Austerweil (*Compt. rend.*, 1924, **178**, 1174—1175).—The separation of camphene from other terpenes (when the former is not present in excess of 30% of the mixture) by crystallisation at a low temperature is rendered impracticable by the formation of eutectic mixtures of low freezing point, which are comparatively rich in camphene. The melting points of a series of mixtures of camphene with α-pinene, β-pinene, mixtures of α- and β-pinene, and dipentene are given. H. J. E.

Melting Points of Mixtures of Camphene and Pinene. E. Darmois (*Compt. rend.*, 1924, **178**, 1546).—Austerweil's conclusion (preceding abstract) that French turpentine contains practically no camphene and that the low melting points of natural camphenes are explained by the presence of small quantities of impurities, was anticipated by the author (A., 1911, ii, 352). J. W. B.

Phellandrenes. II. H. G. Smith, P. G. Carter, and J. Read (*J. Chem. Soc.*, 1924, **125**, 930—940; cf. *ibid.*, 1923, **123**, 1657).—By solution in carbon disulphide, in which the α-nitrite is relatively insoluble, and fractional precipitation, the β-nitrite of *l*-α-phellandrene has been prepared from the essential oils of *Melaleuca acuminata*, *Eucalyptus dives*, and *E. phellandra* in a much higher state of purity than has hitherto been attained. The process of separation can only be controlled effectively by considering the melting points of the various fractions in association with the corresponding rotatory powers. The β-nitrite, m. p. 105—106°, is crystallographically indistinguishable from *l*-α-phellandrene α-nitrite, and has $[\alpha]_D^{20}$ −160° when freshly dissolved in chloroform, the values previously recorded being −36° (Schreiner, A., 1901, i, 600) and −40·82° (Wallach, A., 1904, i, 1035). The striking mutarotative changes of the β-nitrite in acetone, benzene, or chloroform solution, particularly in the presence of piperidine, are similar to those previously observed with the α-nitrite, but optical inversion only takes place in acetone solution. The α- and β-nitrites yield chemically and optically identical specimens of nitro-α-phellandrene and carvotanacetone ($\Delta^{5,6}$-menthen-3-one), and are thus both derived from *l*-α-phellandrene. It is probable that the low rotatory powers of the terpene fractions obtained from eucalyptus oils of the "peppermint group" are due to the presence of partly racemised *l*-α-phellandrene, and a similar remark applies to the essential oil of *Melaleuca acuminata*. R. B.

Oil of Turpentine extracted from the Firs of Bucovina. O. CZERNY (*Bul. Soc. Chim. România*, 1924, **6**, 39—41).—By submitting the greenish-yellow oil obtainable from the bark of the tree to distillation in a current of steam, an oil was obtained which after treatment with sodium hydroxide and subsequent distillation underdiminished pressure, had b. p. 155—216°, d^{16} 0·875, $[\alpha]_D$ −39·2°, acid value 124, saponification value 107, esterification value 13. It was separated by fractional distillation into pinene, a mixture of sylvestrene and dipentene, an ester which on hydrolysis with alcoholic potassium hydroxide yielded borneol, and, probably, a sesquiterpene. The non-volatile residue from the steam distillation, amounting to some 75% of the total weight, was a hard, brittle solid, m. p. 55°, which on distillation yielded traces of acetic and succinic acids and a large amount of coloured oils of very low oxygen content. A. E. C.

Refractive Index of Gums. A. MALLOCK (*Nature*, 1924, **113**, 643).—A corrected table of refractive indices of certain organic solvent liquids and gums is given. A. A. E.

Method for obtaining Pure Glucosides Soluble in Water from Plants. S. GHOSH (*J. Amer. Pharm. Assoc.*, 1923, **12**, 1080—1081).—Steam is passed into an aqueous extract of the bark to which lead chloride and oxide have been added; lead remaining in solution after addition of sodium carbonate and filtration is removed with hydrogen sulphide. Sodium chloride can, if necessary, be removed from the product obtained on evaporation by recrystallisation from ethyl alcohol. CHEMICAL ABSTRACTS.

Nature of the Methyl Salicylate Glucoside present in the Bark of *Betula lenta*. M. BRIDEL (*Compt. rend.*, 1924, **178**, 1310—1312).—The glucoside isolated by Schneegans and Gerock (A., 1895, i, 109) from the bark of *Betula lenta* and named gaultherin yields, not merely methyl salicylate and dextrose, but also xylose, on hydrolysis. It is, indeed, identical with the author's monotropitin (A., 1923, i, 1275), and it is suggested that the latter name be retained and gaultherin discarded. T. H. P.

Biochemical Resolution of Rutin. Formation of a New Glucide, Rutinose. C. CHARAUX (*Compt. rend.*, 1924, **178**, 1312—1314).—The formation of rhamninose by the action of rhamninase on rutin (cf. Ter Meulen, A., 1911, i, 391) is questioned. From the defatted, dehusked seeds of *Rhamnus utilis* the author has obtained, by maceration with water followed by precipitation with alcohol, an enzyme which hydrolyses rutin with formation of quercetin and of a new sugar, termed *rutinose*. The latter is hygroscopic and has no sharp melting point, softening at about 140° and becoming liquid and darkening at 189—192°. It reduces Fehling's solution and exhibits mutarotation in aqueous, but not in alcoholic, solution. When hydrolysed by means of dilute hydrochloric acid, it yields rhamnose (1 mol.) and dextrose (1 mol.).

The same enzyme hydrolyses: robinin, giving a glucide composed of rhamnose (2 mols.) and galactose (1 mol.); a yellow glucoside

obtained from the flowers of *Spiræa ulmaria*, yielding a glucide (apparently different from rutinose), xanthorhamnin, primeverin, baptisin, helicin, and amygdalin. It is without action on *iso*-hesperidin. T. H. P.

Plant Pigments. I. Yellow Colouring Matter of the Acacias. J. M. PETRIE (*Proc. Linnean Soc. N.S. Wales*, 1923, **48**, 356—367).—The soluble colouring matter of the yellow inflorescence of *Acacia discolor*, *A. linifolia*, *A. decurrens* (var. *mollis*), and *A. longifolia* is a rhamnose glucoside of kaempferol, fine, hair-like crystals. No free flavinol was found; the yellow flavinol (0·06%) on reduction with nascent hydrogen gave a red solution resembling that of the natural anthocyanilidine. Carotene and xanthophyll (0·14—0·3%) were present as plastid pigments. The tannins were composed of phloroglucinol, protocatechuic and gallic acids, and on hydrolysis gave red phlobaphen anhydrides.

CHEMICAL ABSTRACTS.

Insecticides. I. Isolation and Constitution of the Active Constituent of Dalmatian Insect Powder. H. STAUDINGER and L. RUZICKA.—(See i, 700.)

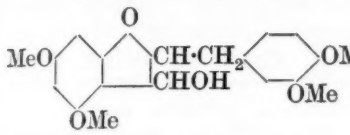
Electrolytic Reduction of Carbonyl Derivatives. H. HIBBERT and R. R. READ.—(See i, 613.)

Humic Acids. H. TROPSCH and A. SCHELLENBERG.—(See i, 619—621.)

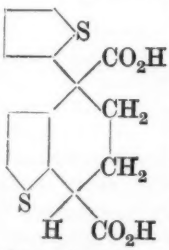
Degradation Product of Brazilin obtained by Schall and Dralle. P. PFEIFFER (*Ber.*, 1924, **57**, [*B*], 738; cf. this vol., i, 413, 537).—Tschitschibabin and Nikitin had already prepared 3-methoxychromanone from the corresponding methoxyphenoxypropionic acid. E. A. M.

Tannins and Similar Substances. XV. A New Degradation of Catechin. K. FREUDENBERG, L. ORTHNER, and H. FIKENTSCHER (*Annalen*, 1924, **436**, 286—298).—The series of reactions which led to the elucidation of the structure of diacetonedextrose and -lævulose (A., 1923, i, 652) has now been applied to the case of catechin. By the action of toluene-*p*-sulphonyl chloride on tetramethyl-*d*-catechin in pyridine solution, the *p*-toluenesulphonic ester, $C_{26}H_{28}O_8S$, m. p. 87—88°, is obtained, which with hydrazine yields: (1) the primary *hydrazide*, $C_{19}H_{24}O_5N_2$ ($+H_2O$, lost *in vacuo* at 65°), m. p. 101—104°, this substance being oxidised by potassium permanganate to give a little tetramethyl-*d*-catechin, m. p. 145°. (2) The highly unstable 3-*mp*-dimethoxyphenylpyrazoline, m. p. 144—145° (*picrolonate*, m. p. 207—208°), which on oxidation with potassium permanganate yields veratric acid, demethylation with hydriodic acid giving a *substance* having m. p. about 240°. (3) Phloroglucinol dimethyl ether, identified as the dibromotrimethyl ether and as

phenacylphloroglucinol dimethyl ether, m. p. 89°. The condensation of veratraldehyde with acetaldehyde in alcoholic potassium hydroxide gives 3 : 4-*dimethoxycinnamaldehyde*, bright yellow, rhombic crystals, m. p. 82—83°, which with hydrazine affords the above 3-*mp*-dimethoxyphenylpyrazoline. The constitution favoured for tetramethylcatechin is that represented by the annexed formula, although two other possibilities are discussed. Dichloropentacetyl-*d*-catechin (*Ber.*, 1880, **13**, 694), when treated with methyl sulphate and methyl-alcoholic potassium hydroxide, affords *dichlorotetramethyl*-d-*catechin*, long, white needles, m. p. 156—157°. R. B.

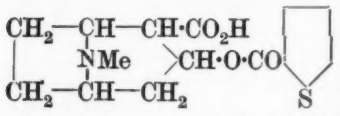


Thiophen Series. XVIII. Synthesis of the "Thiophen-isologue" of Atropine. W. STEINKOPF and A. WOLFRAM (*Annalen*, 1924, **437**, 22—36).—Ethyl thienyl-2-glyoxylate (b. p. 138—140°/13 mm.) was prepared by treating thiophen with ethyl oxalic chloride (cf. Scholl and Egerer, A., 1913, i, 588) in presence of aluminium chloride. With magnesium methyl bromide, it gives *ethyl α-hydroxy-α-2-thienylpropionate*, an oil, b. p. 134—135°/13 mm., readily hydrolysed by barium hydroxide to the corresponding *acid*, needles, m. p. 107°. When alkali hydroxide is used as hydrolysing agent, side reactions take place and an amorphous product resembling that described below is obtained. It was found impossible to isolate α-2-thienylacrylic acid; the above hydroxy-acid, treated with acid in various ways, gives solely a mixture of two *isomerides*, one amorphous (decomp. 95°), the other crystalline, m. p. 216°. The latter, termed di-α-thienylacrylic acid, has properties which suggest that it has the annexed formula. The amorphous substance was also obtained as a by-product in the preparation of β-*chloro-α-2-thienylpropionic acid*, which was eventually isolated by treating α-hydroxy-α-2-thienylpropionic acid with hydrogen chloride in ether solution at −40° to −30°. It forms rhombs, m. p. 77°. Hydrolysed with calcium carbonate, it gives β-*hydroxy-α-2-thienylpropionic acid*, prisms, m. p. 95·5—96°, the *acetyl* derivative of which is oily, and when treated with thionyl chloride yields β-*acetoxy-α-2-thienylpropionyl chloride*, also an oil. Tropine with the latter compound in benzene solution affords β-*hydroxy-α-2-thienylpropionyltropine*, "*thiophen-cocaine*" (*chloroplatinate*, decomp. 240—241°, and *picrate*, m. p. about 142°, described). The quantity obtained was insufficient for pharmacological tests. W. A. S.

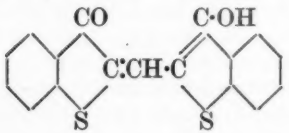
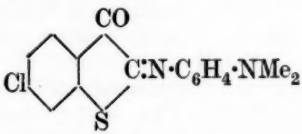


Thiophen Series. XVII. Preparation of the "Thiophen-isologue" of Cocaine. W. STEINKOPF and W. OHSE (*Annalen*, 1924, **437**, 14—22).—"Thiophen-cocaine" was obtained by methylating the product of interaction of ecgonine and thiophen-2-carboxylic anhydride. Thiophen-2-carboxylic acid is best pre-

pared (yield: 96%) from 2-bromothiophen (Steinkopf, A., 1923, i, 124) by the Grignard reaction (cf. Schlenk and Ochs, A., 1915, i, 579). The best yield (62%) of 2-cyanothiophen, the intermediate in an alternative preparation of the acid, was obtained when cyanogen chloride was used; the bromide, iodide, and cyanogen itself gave poor yields (cf. Karrer and others, A., 1919, i, 591). Thiophen-2-carboxylic acid heated with acetic anhydride yields the *anhydride*, needles, m. p. 62°, b. p. 218—220°/15 mm., rapidly reacting in warm aqueous suspension with ecgonine to give *thiophen-2-carboxyecgonine* (annexed formula), which sinters at 94°, solidifies and melts at 186°, and has $[\alpha]_D^{17.5}$ −19·07° to −17·49° in chloroform. Its *hydrochloride* has m. p. 225° (decomp.). The *methyl* ester, viz. "*thiophen-cocaine*," has m. p. 107°; its *hydrochloride*, m. p. 184·5°, the *picrate*, yellow needles, m. p. 175°, and *chloroplatinate* are described. Pharmacologically the substance closely resembles cocaine but appears to be less toxic. W. A. S.

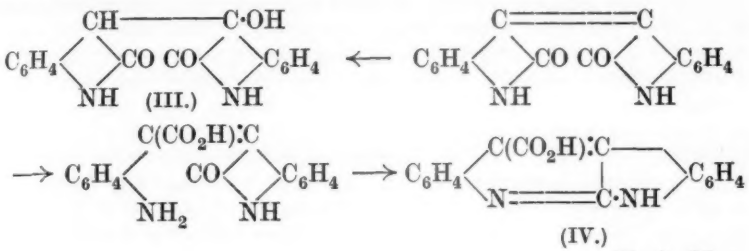


Fission of Indigoid Dyes by Alkalis. P. Friedländer and L. Sander (*Ber.*, 1924, 57, [*B*], 648—652; cf. A., 1922, i, 764).—Thioindigotin when heated with 45% potassium hydroxide and a little alcohol is converted into oxythionaphthen, thionaphthenquinone, and a little of the known substance (I). 6 : 6′-Dichloro-

(I.)   (II.)

thioindigotin is much more resistant to the above treatment and affords 6-chloro-3-oxy(1)thionaphthen (colourless needles, m. p. 143°) (cf. Ruppel, *Dissert.* Darmstadt, 1921), and 6-*chlorothionaphthenquinone*. The latter (orange needles, m. p. 134°) was also prepared by condensing the chloro-oxythionaphthen with *p*-nitrosodimethylaniline, the resulting 6-*chlorothionaphthenquinone*-p-*dimethylamino*-2-*anil* (II) (dark green, metallic prisms, m. p. 190°) being hydrolysed by hydrochloric acid. 6 : 6′-Dichloro-4 : 4′-dimethylthioindigotin, on treatment with alkali, gives only a trace of 6-*chloro*-4-*methylthionaphthenquinone*, orange needles, m. p. 132°, which was also prepared from the *anil*, m. p. 123·5°. *iso*Indigotin has been prepared by an improved method (due to B. Homolka) from isatin and an aqueous solution of sodium sulphide and ammonia. It is converted by hot aqueous-alcoholic sodium hydroxide into *hydroxydihydroisoindigotin*, (III), colourless leaflets or needles, m. p. 250—280° (decomp.) (converted by hot acetic anhydride into diacetyl-*iso*indigotin), and *quinindolinecarboxylic acid* (IV), yellow needles (*sodium* salt, $C_{16}H_9O_2N_2Na,3H_2O$, yellow needles), a little isatin and other substances also being formed. The acid, when heated at 300°, affords quinindoline (cf. Gabriel and Eschenbach, A.,

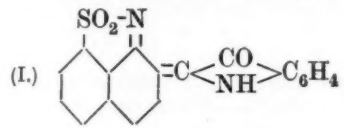
1898, i, 199). The decomposition by alkali probably occurs as shown below :



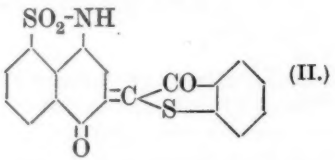
(III.) (IV.)

F. A. M.

Indigoid Dyes. P. FRIEDLÄNDER and L. SANDER (*Ber.*, 1924, 57, [*B*], 637—648).—The following new indigoid dyes are described : the *dye* (I) from naphthasultam and isatinanilide by condensation in presence of acetic anhydride, forms deep bluish-violet needles with red iridescence which give a yellow solution in alkali.



(I.)



(II.)

The condensation of 3-oxy(1)thionaphthen with naphthasultamquinone in acetic acid yields a *dye* (II) which forms purple-black needles. No dye could be obtained on attempting to condense isatinanilide with the *p*-tolylsulphamide of α-naphthylamine, although the latter couples with diazo compounds in alkaline solutions. A re-examination of the "2-dihydronaphthalene-2′-indoleindigo" described by Herzog and Kreidl (A., 1923, i, 61) showed that their product was probably an impure "2-naphthalene-2-indoleindigo." The substance described by Herzog and Kreidl as 1-keto-2 : 3′-oxy-2′-thionaphthentetrahydronaphthalene may, however, have the structure ascribed to it, although analysis alone is insufficient to determine the presence or absence of the two hydrogen atoms; on warming with concentrated aqueous-alcoholic sodium hydroxide, it forms a yellow solution from which acetic acid precipitates a yellow, amorphous *additive* compound with water possibly $C_{10}H_8O{:}C(OH)\cdot CO\cdot C_6H_4\cdot SH$. Above 100°, the dye is re-formed; the hydrated compound behaves like an enol and like a mercaptan. 6-*Ethoxythionaphthenquinone*-2-*anil* was prepared from 6-ethoxythionaphthen and nitrosobenzene as yellow needles, m. p. 118—119°. It condensed with α-ketotetrahydronaphthalene in acetic anhydride to give the brownish-red dye, "3 : 4-*dihydro*-2-*naphthalene*-6′-*ethoxy*-2′-*thionaphthenindigo*." 2-*Chloro*-1 : 4 *naphthaquinone monoanil* was obtained by condensing 2-chloro-α-naphthol with nitrosobenzene in presence of ammonia as fiery red needles, m. p. 112°; it was not possible to obtain an indigoid dye

from it by condensation with oxythionaphthen; by using sodium hydroxide in the above condensation in place of ammonia, the product was almost entirely Euler's anilinonaphthaquinone-monoanil, the chlorine atom being removed. The following *acyl* derivatives of indigoid dyes were also prepared: "N-*Acetyl*-2-*indole*-2'-*thionaphthenindigo*," from the corresponding indigoid dye, acetic anhydride, and acetyl chloride, forms light red needles; *di*(N-*acetyl*)iso*indigotin*, obtained similarly from *iso*indigotin, forms brick-red crystals. N : N'-*bis*(*chloroacetyl*)*indigotin* was obtained from indigotin and chloroacetyl chloride as ruby-red, quadratic, double pyramids; it is sensitive to water-vapour and gradually becomes coated with indigotin; "4-*acetylamino*-2-*naphthalene*-2'-*indoleindigo*" is a violet-blue product, and "4-*acetylamino*-2-*naphthalene*-2'-*thionaphthenindigo*" reddish-violet. Treatment of indigotin with oxalyl chloride in boiling nitrobenzene afforded *oxalylindigotin* as yellow needles, m. p. above 200°. It is extremely easily hydrolysed by dilute alkali with regeneration of indigotin and is sulphonated by warm fuming acid (20% SO_3). These observations confirm Friedländer's view (A., 1922, i, 765) that saturation of the nitrogen atoms in indigoid dyes leads to lightening of the colour. F. A. M.

Derivatives of 3-Oxy(1)thionaphthen. L. R. Hart and S. Smiles (*J. Chem. Soc.*, 1924, **125**, 876—881).—*o*-Thiolbenzoic acid condenses with compounds containing a labile methylene group to give 3-oxythionaphthen derivatives (cf. T., 1923, **123**, 2907), but in no case are 2 : 2-disubstituted derivatives formed; one of the groups originally attached to the methylene group is always displaced, and if this cannot happen the reaction does not take place. *o*-Thiolbenzoic acid and oxalacetic, acetylpyruvic, or pyruvic acid react in sulphuric acid solution to give 3-*oxy*(1)*thionaphthen*-2-*glyoxylic acid*, $C_6H_4<^{CO}_{S}>CH\cdot CO\cdot CO_2H,H_2O$, m. p. 174° when anhydrous. The *calcium* salt is described. The *phenylhydrazone* forms orange needles, m. p. 187°, and the *anil* yellow plates, m. p. 190°. The o-*amino-anil* forms yellow prisms (converted into the following compound before melting). When *o*-phenylenediamine and the acid were mixed in boiling acetic acid, "2-*thionaphthen*-2-*quinoxalineindigo*," $C_6H_4<^{CO}_{S}>C:C<^{CO-NH}_{NH\cdot C_6H_4}$, was readily formed as a red, crystalline powder not melting below 315°. 2-*Benzoyl*-3-*oxy*(1)*thionaphthen* was produced by condensation of *o*-thiolbenzoic acid and benzoylacetone; it forms orange or pale yellow needles, m. p. 116—117°. Its *phenylhydrazone* crystallises in orange plates, m. p. 160°. Its acetyl derivative, 2-*benzoyl*-3-*acetoxy*(1)*thionaphthen*, forms needles, m. p. 106°. 2-*Acetyl*-3-*benzoyloxy*(1)*thionaphthen*, formed by benzoylating 2-acetyl-3-oxythionaphthen, has m. p. 145°. The disinclination to form 2 : 2-disubstituted derivatives is again shown here. 2-*Benzoyl*-3-*benzoyloxy*(1)*thionaphthen* crystallises in plates, m. p. 113°. W. A. S.

Constitution of Evodiamine and Rutæcarpine. Y. ASAHINA (*J. Pharm. Soc. Japan*, 1924, No. 503, 1—7; cf. Asahina and Mayeda, A., 1921, i, 48).—Indole-β-ethylamine (3-aminoethylindole) is obtained by the decomposition of evodiamine. The constitutions of evodiamine and rutæcarpine are, therefore, as stated by Kermack, Perkin, and Robinson (T., 1921, **119**, 1615). K. K.

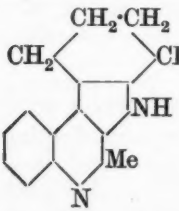
Methylation of Tertiary Amines and Alkaloids by means of Methyl Sulphonic Esters derived from Phenols. L. J. SIMON and M. FRÉREJACQUE (*Compt. rend.*, 1924, **178**, 945—947).—When treated with methyl iodide or sulphate or with one of various sulphonic esters derived from aromatic hydrocarbons, hexamethylenetetramine yields the salt of a quaternary methylated base, one methyl group being fixed by a tertiary nitrogen atom: $C_6H_{12}N_4+R\cdot OMe=C_6H_{12}N_3(NMe)\cdot OR\longrightarrow C_6H_{12}N_3\cdot NMe\cdot OH$. This reaction is effected very readily and completely by the methyl sulphonates derived from phenols (A., 1923, i, 462, 1098), giving the phenolsulphonates of the same base. The reaction is best carried out in chloroform solution and, even in the cold, is extremely sensitive, 0·02 g. of hexamethylenetetramine rapidly yielding the characteristic crystalline compounds. The *compounds* obtained, with their approximate decomposition temperatures, are as follows: $OH\cdot C_6H_4\cdot SO_3Me$ [1 : 4], 225°; $OH\cdot C_6H_3Me\cdot SO_3Me$ [2 : 1 : 5], 134°; $OH\cdot C_6H_3Me\cdot SO_3Me$ [OH : Me=1 : 4], 175°; $OMe\cdot C_6H_4\cdot SO_3Me$ [1 : 4], 195°; $OMe\cdot C_6H_3Me\cdot SO_3Me$ [2 : 1 : 5], 190°; $OMe\cdot C_6H_3Me\cdot SO_3Me$ [OMe : Me=1 : 4], 215°; $OH\cdot C_6H_3(CO_2Me)\cdot SO_3Me$ [OH : CO_2Me= 2 : 1], 230°. These salts yield the corresponding *picrates* when treated with picric acid in aqueous solution.

Compounds of similar type are obtainable from antipyrine, pyramidone, dimethylaniline, and pyridine, a solvent other than chloroform being sometimes necessary. The products obtained from antipyrine by means of the methyl sulphonates of methyl salicylate and anisole have m. p. 135° and 96°, respectively. The salt formed from pyramidone and methyl anisolesulphonate has m. p. 162°, and that from pyramidone and dimethyl sulphosalicylate, m. p. 97°. The reaction is applicable also to the alkaloids. T. H. P.

Kinetics of Catalytic Dehydrogenation. II. N. ZELINSKY and G. PAWLOW (*Ber.*, 1924, **57**, [*B*], 669—671; cf. A., 1923, i, 767).—Palladium is a much more active catalyst than platinum in effecting the dehydrogenation of piperidine, which, with the first metal, only follows a normal course at temperatures below 250°; at higher temperatures the catalyst becomes partly inactivated owing to subsidiary reactions. The phenomenon is due to the chemical nature of piperidine, since the dehydrogenation of *cyclo*hexane (*loc. cit.*) occurs normally within much wider limits of temperature. With piperidine, as with *cyclo*hexane, dehydrogenation commences at about 150°; between 150° and 200°, piperidine is much more energetically dehydrogenated by palladium than is *cyclo*hexane. H. W.

Spectrochemistry of Heterocyclic Nitrogen Compounds. K. VON AUWERS and W. KOHLHAAS (*Annalen*, 1924, **437**, 36—63).—Densities and refractivities for the α, He, β, and γ lines at various temperatures are recorded for pyrrole, 1-methylpyrrole, 2 : 4- and 2 : 5-dimethylpyrroles, and 2 : 3 : 5-trimethylpyrrole; for 26 pyrazole compounds, including 3 : 5-*dimethylpyrazole*, m. p. 58° (*picrate*, m. p. 153°); 4-*chloro*-1-*phenyl*-3 : 5-*dimethylpyrazole*, b. p. 162—165°/10—11 mm.; for 20 derivatives of tetrahydroindazole (cf. this vol., i, 325) and for 21 of indazole itself (cf. also A., 1921, ii, 73; 1922, ii, 98). W. A. S.

Mechanism of E. Fischer's Synthesis of Indoles. Application of the Method to the Preparation of a Pyrindole Derivative. G. M. ROBINSON and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 827—840).—Largely polemical against Hollins (A., 1922, i, 863). Reddelien's explanation of the reaction (A., 1912, i, 263), involving as it does an oxidation and scission of the hydrazone as an intermediate stage, is untenable because, in the first place, tetrahydrocarbazole may be obtained from *cyclo*hexanonephenylhydrazone even when stannous chloride is present in the reaction mixture, and, secondly, 2-methylindole, or nitrotetrahydrocarbazole, is produced normally even when *p*-toluidine, or aniline, respectively, is added to supply, on Reddelien's hypothesis, an alternative base. Further, *N*-methyltetrahydrocarbazole is the sole product of the action of hot acetic acid and aniline (20 mols.) on *cyclo*hexanonephenylmethylhydrazone. Thus the authors' original theory (A., 1918, i, 448) is substantiated. The same general method has been applied to the synthesis of a pyrindole derivative (cf. Fargher and Furness, A., 1915, i, 842). 3-*Hydrazinoquinaldine*, prepared by reducing diazotised 3-aminoquinaldine, first with sodium hydrogen sulphite, then with the hyposulphite, forms pale yellow needles, m. p. 169°. *Benzaldehydequinaldyl*-3-*hydrazone* crystallises in yellow plates, m. p. 202°, its *hydrochloride* in needles, m. p. 261°. *cyclo*Hexanonequinaldyl-3-hydrazone has m. p. about 100° in the crude (colourless) condition, but when recrystallised is converted into an orange *dioxide*(?), needles, m. p. 131° (decomp.). This yields 3-quinaldineazo-β-naphthol when fused with β-naphthol and generally behaves remarkably like quinaldine-3-diazo-4-oxide (Conrad and Limpach, A., 1888, 1109). By treating quinaldylhydrazine with a large excess of *cyclo*hexanone, 3-*methylbenzo*-(5 : 6-)9 : 10 : 11 : 12-*tetrahydro*-4-*carboline* (annexed formula) was obtained. This substance crystallises from benzene in needles, m. p. 198°, containing benzene (1 mol.), which is lost at 140—150°, the substance then melting at 226°. Its *methosulphate* has m. p. 225°; treated with potassium hydroxide, it yields 3 : 4-*dimethylbenzo*-(5 : 6-)9 : 10 : 11 : 12-*tetrahydro*-4-*isocarboline*, yellow needles, m. p. 120° (decomp.). *cyclo*Hexanone interacts with hydrazine itself to form an azine (cf. Mailhe, A., 1922, i, 332), which with zinc chloride forms a *compound*,



$C_{12}H_{20}N_2,HCl,ZnCl_2$, colourless prisms, m. p. 271—272°. Certain analytical figures relating to the compound obtained from cotarnine and 6-nitropiperonal are corrected (cf. T., 1914, **105**, 1468).

W. A. S.

Intramolecular Condensation Reactions of Aminoaldehydes and Aminoacetals. II. Course of the Reaction in the Formation of Dihydroquinoline and a New Preparation of Indole Derivatives. C. Räth (*Ber.*, 1924, **57**, [*B*], 715—718; cf. this vol., i, 555).—When *o*-aminopropylbenzene is heated with chloroacetal at 250° the expected 4-*ethyl*-1 : 2-*dihydroquinoline*, a pale yellow oil (b. p. 125—135°) with slightly tarry odour (*hydrochloride*, pinkish, hygroscopic, and amorphous), is formed together with 3-*ethoxy*-4-*ethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, a yellow, viscous oil (b. p. 180—185°/21 mm., or 175—185°/17 mm.). β-Chloropropionacetal and aniline when heated together at 250° give a little dihydroquinoline and (mainly) 4-*ethoxytetrahydroquinoline*, a yellowish-brown, viscous oil (b. p. 264—270°), which darkens in air (*picrate*, fine, yellow needles). 3-*Ethoxy*-1-*ethyl*-2 : 3-*dihydroindole* (*hydrochloride*, amorphous), a thick, yellow liquid, b. p. 153—163°/11 mm., is obtained from ethylaniline and bromoacetal, although the chief product in this case is 1-ethylindole.

F. A. M.

Synthesis of 2 : 4 : 7- and 2 : 4 : 8-Trimethylquinolines. S. Yamaguchi (*J. Pharm. Soc. Japan*, 1924, No. 503, 8—33).—The author has synthesised 2 : 4 : 7- and 2 : 4 : 8-trimethylquinolines and their salts, from acetone, paraldehyde, and *m*- and *o*-toluidines, respectively. Generally speaking, 2 : 4 : 6- and 2 : 4 : 7- but not 2 : 4 : 8-derivatives have a large affinity for water and for methyl iodide.

2 : 4 : 8-Trimethylquinoline is a white solid, m. p. 42°, b. p. 269—270°, and gives the following salts: *hydrochloride*, m. p. 238°; *hydrobromide*, m. p. 251° (decomp.); *hydriodide*, m. p. 224°; *chloroaurate*, m. p. 191°; *chloroplatinate*, m. p. 275° (decomp.); *mercurichloride*, m. p. 234°; *zincichloride*, m. p. 295—296° (decomp.); *hydrogen sulphate*, m. p. 263°; *dichromate*, decomp. at about 180°; *picrate*, m. p. 193°; methiodide, m. p. 229° (decomp.).

2 : 4 : 7-Trimethylquinoline is a colourless, oily liquid, b. p. 280—281°, d^{20} 1·0337, n_D^{24} 1·59732. On exposure to air, or when crystallised from water, it forms a crystalline *hydrate*, m. p. 48°. The following salts are described: *hydrochloride*, sublimes at about 310°; hydrobromide, m. p. 351° (decomp.); *hydriodide*, m. p. 320° (decomp.); *chloroaurate*, m. p. 152°; *chloroplatinate*, m. p. 272° (decomp.); *mercurichloride*, m. p. 244°; *zincichloride*, m. p. 258°; *hydrogen sulphate*, m. p. 223°; *dichromate*, decomp. at about 179—180°; *picrate*, decomp. 232°; methiodide, subliming at about 322°.

K. K.

Relations between Chemical Constitution and Taste. (Miss) C. Riccomanni (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 145—148).—1 : 4-Di-δ-phenyl-Δ$^{\delta}$-pentenoylpiperazine, prepared by heating piperazine at 100—105° with δ-phenyl-Δ$^{\delta}$-pentenoic acid (cf.

Staudinger and Schneider, A., 1923, i, 361; Staudinger and Müller, A., 1923, i, 363), is obtained as a dense, brownish-yellow oil with a pungent, aromatic taste, yields a yellow *picrate*, m. p. 245°, and when mixed in the proportion of 2% with flour produces a taste similar to, although less intense than, that of pepper. Evidently piperidine is not necessary for obtaining the flavour of pepper.

When added in the proportion of 1% to flour, styryl methyl ketone exhibits a markedly sharp taste (cf. Nomura, T., 1917, i, 769; A., 1918, i, 446; Nomura and Nozawa, A., 1918, i, 438); cinnamylidenemethyl methyl ketone has an intense, biting taste which appears after a time; benzyl methyl ketone has also an acute taste and acetophenone a pungent taste which disappears almost immediately. With compounds which lack the phenyl group or which contain a partly hydrogenated aromatic ring, such as ionone, the acute taste disappears almost completely.

2-Acetylpyrrole, 2-pyrryl styryl ketone, and the product of the condensation of cinnamaldehyde with 2-acetylpyrrole,

$$C_4H_4N\cdot CO\cdot CH{:}CH\cdot CH{:}CHPh,$$

have sweet, and in no way pungent, tastes. T. H. P.

Preparation of New Salts of CC-Disubstituted Barbituric Acids. E. Layraud (Brit. Pat. 202660).—New salts are obtained by mixing hot aqueous solutions of *as*-CC-disubstituted barbituric acids and piperazine. *Piperazine ethylbutylbarbiturate* melts at about 150—155°. The piperazine salts (acid : base=1 : 1 mol.) afford stable aqueous solutions. *Salts* are also obtained by treating ethyl*iso*butyl-, ethyl*iso*amyl-, propylbutyl-, propyl*iso*butyl-, and propyl*iso*amyl-barbituric acids with either an organic base, other than piperazine, or an inorganic base, other than sodium.

W. T. K. B.

Synthetic Hypnotics of the Barbituric Acid Series. A. W. Dox (*J. Amer. Pharm. Assoc.*, 1923, **12**, 602—609).—A consideration of the nature of the group producing hypnotic effect. In the veronal class, the group $\cdot CR_2\cdot CO\cdot NH\cdot CO\cdot$ is a "hypnophore." Macht's "specific benzyl effect" is simply a higher alcohol effect. To manifest hypnotic action without undesirable after-effects, the two 5-alkyl groups of the pyrimidine ring should together contain between 4 and 8 carbon atoms; at least one such group must be of open-chain form. The benzyl group is undesirable, the carbamide group may not be replaced by the amidine group, and the molecular weight should not exceed about 250. Chemical Abstracts.

Hypnotic and Analgesic Compounds from Dimethylaminophenyldimethylpyrazolone and Dialkylbarbituric Acids. E. H. Volwiler (U.S. Pat. 1478463).—Yellow or orange-yellow, crystalline compounds, m. p. 94·5—96·5°, 88—90°, 84—86°, and 90—94°, are produced from dibutyl-, ethylbutyl-, ethyl*sec.*butyl-, and ethyl*iso*amyl-barbituric acids, respectively. *Ethylsec.butylbarbituric acid* is obtained by condensing ethyl ethyl*sec.*butylmalonate (b. p. 133°/48 mm.) with carbamide in the presence of sodium ethoxide. Chemical Abstracts.

Mother Substance of Indian-yellow. F. MAYER (*Arch. Exp. Path. Pharm.*, 1924, **101**, 383—385).—The formulæ proposed by Wiechowski (A., 1923, i, 591) for mangin and euxanthone are at variance with the accepted conclusions of Fischer and Piloty (A., 1891, i, 677) and other workers; they are therefore to be regarded as erroneous. W. O. K.

Constitution of Pyrazoles, Indazoles, and Anthranils. K. VON AUWERS (*Annalen*, 1924, **437**, 63—86).—A discussion of the bearing of data previously obtained (see i, 666) on the constitution of these compounds. To assist in calculating atomic refractivities for singly-linked or doubly-linked nitrogen, refractivity measurements were made on eleven substituted hydrazines, whilst the constants for five more indazole derivatives, anthranil itself, and three substituted anthranils are also recorded. The author's conclusion is that none of the indazole compounds contains a 3-membered ring structure and that the 1- and 2-derivatives differ only in the arrangement of the double bonds. Anthranil and related compounds should be formulated as analogous to indazole, not as internal amides. W. A. S.

Sulphonation of Glyoxalines. II. R. FORSYTH, J. A. MOORE, and F. L. PYMAN (*J. Chem. Soc.*, 1924, **125**, 919—923).—Attempts to remove the methyl group from 2-methylglyoxaline-4-sulphonic acid so as to determine the constitution of glyoxalinesulphonic acid (T., 1920, **117**, 1429) failed. Oxidising agents either did not act or completely disrupted the molecule. A benzylidene compound was not formed. When glyoxaline is treated with 70% oleum at 160° for 36 hours the product contains 15% of a *disulphonic acid*. 2-Methylglyoxaline, similarly treated for 3—6 hours, gives *2-methylglyoxaline-4-sulphonic acid*, $C_4H_5N_2 \cdot SO_3H, H_2O$, prisms, m. p. (decomp.) about 279° when anhydrous. The *ammonium*, *barium*, and *sodium* salts are described. In some experiments, a small proportion (up to 17%) of the 4 : 5-*disulphonic acid* was produced. This forms needles containing $1 \cdot 5H_2O$ and has m. p. 280°; its *barium* salt is described. Neither glyoxalinesulphonic acid nor methylglyoxalinesulphonic acid afforded esters or chlorides. Partial hydrolysis took place when they were heated at 170° with concentrated hydrochloric acid. Treated with bromine (1 mol.) in aqueous solution, glyoxalinesulphonic acid gives ammonium bromide, oxalic acid, and 2 : 4 : 5-tribromoglyoxaline, 65% of the acid being recovered unchanged; methylglyoxalinesulphonic acid behaves similarly, yielding a little 4 : 5-dibromo-2-methylglyoxaline and 4-bromo-2-methylglyoxaline-5-sulphonic acid (cf. Light and Pyman, T., 1922, **121**, 2626). W. A. S.

Indoleninocyanines [Indocyanines]. W. KÖNIG [with E. WAGNER] (*Ber.*, 1924, **57**, [*B*], 685—692; cf. A., 1923, i, 1188).—1 : 2 : 3 : 3-Tetramethylindolenium iodide is converted by ethyl orthoformate in boiling acetic anhydride solution into 1 : 3 : 3 : 1′ : 3′ : 3′-*hexamethyl*streptomonovinylene-2 : 2′-*indocyanine iodide* (annexed formula), golden needles, m. p. about 229° (decomp.).

The corresponding *bromide*, m. p. 250° (decomp.), *chloride*, decomp. 250°, *perchlorate*, m. p. 245° (decomp.), and *picrate*, m. p. 205°, are described. The new dye is remarkable among quinocyanines on account of its relatively great stability towards mineral acids and light. It is converted by a very large excess of sodium hydroxide into the corresponding pale yellow *ψ-base*, m. p. about 96° (decomp.), which when suspended in water passes into equilibrium with the red onium base. *5-Chloro-1 : 2 : 3 : 3-tetramethylindolenium iodide*, pale yellow needles, m. p. 198°, prepared by fusing acetone-*p*-chlorophenylhydrazone with zinc chloride, is converted in a similar manner into *5 : 5′-dichloro-1 : 3 : 3 : 1′ : 3′ : 3′-hexamethylstreptomonovinylene-2 : 2′-indocyanine iodide*, needles, m. p. 265°; the corresponding *carbinol base*, a pale yellow, amorphous substance, has m. p. about 130° (decomp.).

H. W.

Preparation of Diaminodiaryldialkylmethanes. FARBW. VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 204722).—Aniline, or a nuclear alkyl-substituted derivative with a free *p*-position, is caused to react, in the form of a salt in aqueous solution, with an aliphatic ketone (*e.g.*, by heating under pressure at 120—150°). *pp′-Diaminodiphenyldimethylmethane*, $CMe_2(C_6H_4{\cdot}NH_2)_2$, forms colourless needles, m. p. 132°. *pp′-Diaminodi-m-tolyldimethylmethane* (from *o*-toluidine and acetone) has m. p. 71°, and *pp′-diaminodiphenylmethylethylmethane* (from aniline and methyl ethyl ketone), m. p. 78°. These compounds are valuable as intermediates for dyes.

W. T. K. B.

Dyes derived from Carbazole and Thiodiphenylamine. S. DUTT (*J. Chem. Soc.*, 1924, **125**, 802—807).—Carbazole condenses with aldehydes and ketones in presence of concentrated sulphuric acid or zinc chloride to form triarylmethane compounds which may be oxidised to dyes. As 3-nitro-, but not 3 : 6-dinitro-, carbazole will so condense it is inferred that substitution takes place in position 3. With formaldehyde the *compound*, $CH_2(C_{12}H_8N)_2$, colourless needles, m. p. 287°, is obtained; benzaldehyde affords the *leuco*-base, $CHPh(C_{12}H_8N)_2$, needles, m. p. above 300°, which, oxidised with nitrosyl chloride in sulphuric acid solution, gives the dark green *chloride* of the dye, the colourless *carbinol base* of which is obtained by boiling with pyridine and forms needles, m. p. above 290°. Similar compounds were prepared using *p*-dimethylaminobenzaldehyde [dark violet needles; *carbinol base*, m. p. 282° (decomp.)], *m*-nitro- and *m*-chloro-benzaldehydes. When sulphonated, all these products dye unmordanted cotton in green to violet shades. Benzophenone, *pp′*-tetramethyldiaminobenzophenone, and 2 : 3 : 4-trihydroxybenzophenone yield (with phosphoryl chloride as condensing agent) *compounds* of the type, $C_{12}H_8N{\cdot}CPh_2Cl$. The *carbinol base* of the first named forms colourless needles, m. p. 172°, and its *chloride* violet needles, m. p. 280—285°; the remainder have m. p.

above 290°. All dye wool in violet shades and the last-named dyes chrome-mordanted textiles dark violet or black shades. Thiodiphenylamine yields analogous derivatives. With oxalic acid, a green *compound*, $C(C_{12}H_8NS)_3 \cdot CO_2H$, giving a colourless *base*, $C(C_{12}H_8NS)_3 \cdot OH$, m. p. 225—227°, was formed. Benzaldehyde (*carbinol base*, decomp. 200°) and *p*-dimethylaminobenzaldehyde gave compounds dyeing cotton green and grey, respectively, from a sulphide bath. *p*-Hydroxy- and *m*-nitro-benzaldehydes also condense. With benzophenone, and its 2 : 3 : 4-trihydroxy and *pp'*-tetramethyldiamino derivatives, compounds were produced which dye wool or unmordanted cotton blue or violet shades. These substances are decomposed by concentrated sulphuric acid. Thiodiphenylamine will also condense with nitrosophenols (*p*-nitrosophenol, *p*-nitroso-*m*-dimethylaminophenol, dinitrosoresorcinol, α-nitroso-β-naphthol, β-nitroso-α-naphthol), giving products which, unlike the carbazole-indophenols, will dye cotton from a hyposulphite or sulphide "vat." By fusion with sodium polysulphide at 250—300°, they yield sulphur dyes giving green, brown, or black shades. Compounds with similar properties are formed with diketones (benzil, phenanthraquinone, isatin). W. A. S.

Preparation of Acylacetyl Compounds. CHEM. FABR. GRIESHEIM-ELEKTRON (Brit. Pat. 211772).—Diacylacetyl compounds are prepared by heating, preferably in a solvent (*e.g.*, a benzene hydrocarbon, chlorobenzene, nitrobenzene, naphthalene, or a large excess of the acylacetic ester used), at least 2 mols. of an acylacetic ester with 1 mol. of a diamine of the general formula $NH_2 \cdot Y \cdot NH_2$, where Y represents an aryl or substituted aryl residue, a diaryl or substituted diaryl residue, or a residue of a diaryl compound of the type –Ar·Z·Ar'–, where Ar and Ar' stand for the same or different aryl or substituted aryl residues united by a connecting link, Z, which may be ·O·, ·S·, ·CH_2·, ·CO·, ·NH·, ·NHCO·, ·N:N·, $O<\begin{matrix}N\cdot\\ |\\ N\cdot\end{matrix}$, ·NH·CO·NH·, ·O·$CH_2$·$CH_2$·O·, or the like. The diacylacetyl compounds have a substantive character, so that they can be fixed on the cotton fibre in alkaline solution and developed with diazo compounds, giving shades which are fast to washing. Details of the preparation of several representatives are given, and the following new compounds described. *Diacetoacetyl*-p-*phenylenediamine*: slender, colourless needles, m. p. 167° (decomp.); *diacetoacetyl*-o-*tolidine*: slender, lustrous needles, m. p. 204—205° (decomp.); *diacetoacetyl*-o-*dianisidine*: feebly yellow needles, m. p. 164—165° (decomp.); *dibenzoylacetyl*-o-*tolidine*: slender, colourless, lustrous needles, m. p. 233° (decomp.); *diacetoacetyl*-4 : 4'-*diaminobenzophenone*: colourless, lustrous needles, m. p. 175—176° (decomp.); *diacetoacetyl*-4 : 4'-*diaminoazobenzene*: orange-yellow, crystalline powder, decomp. 233—234°; *diacetoacetyl*-1 : 4-*naphthylenediamine*: colourless needles, m. p. 197° (decomp.); *diacetoacetyl*-1 : 5-*naphthylenediamine*: silvery scales, m. p. 249—250° (decomp.); *diacetoacetyl*-2 : 6-*naphthylenediamine*: lustrous needles, m. p. 203—204° (decomp.); *diacetoacetyl*-o : o'-*dichloro*-

benzidine: colourless, crystalline flocks, decomp. 145—147°; *diacetoacetyl*-m : m′-*dichlorobenzidine*: colourless needles, decomp. 212°; *dibenzoylacetylbenzidine*: yellow, crystalline powder, m. p. 248° (decomp.); *diacetoacetyl*-4 : 4′-*diamino*-3 : 3′-*dichlorodiphenylmethane*: colourless, small crystals, m. p. 138—139° (decomp.); *diacetoacetyl*-4 : 4′-*diamino*-3 : 3′-*ditolylmethane*: colourless, felted needles, m. p. 143—144° (decomp.); *diacetoacetyl*-4 : 4′-*diaminoazoxybenzene*: brownish-yellow, crystalline powder, m. p. 219—220° (decomp.); *diacetoacetyl*-4 : 4′-*diamino*-3 : 3′-*azotoluene*: bright yellow powder, m. p. 215° (decomp.); *diacetoacetyl*-4 : 4′-*diaminodiphenylcarbamide*: colourless, lustrous leaflets, melting above 320°. W. T. K. B.

Preparation of [Azo] Dyestuffs derived from Pyrazolone and of Intermediate Products therefor. Society of Chemical Industry in Basle (Brit. Pat. 210669).—1-Aryl-5-pyrazolones are prepared by condensing the hydrazine derivative of an aromatic primary amine containing a sulphonamido group (*e.g.*, 3-aminobenzene-1-sulphonamide) with a suitable derivative of a β-ketonic acid (*e.g.*, ethyl acetoacetate or ethyl oxaloacetate). By coupling these pyrazolones with a diazo compound, azo dyes are obtained which are remarkable for their uniformity and purity of tint (yellow to red). More particularly is this the case with the mordant dyes obtained by coupling the new pyrazolones with diazo derivatives of *o*-aminophenol and *o*-aminonaphthol, and especially with the acid dyes containing chromium produced by treating these mordant dyes with a chroming agent (*e.g.*, chromium formate). [Cf. *B.*, 1924, 412.] W. T. K. B.

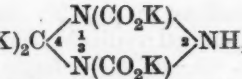
Scission of Disulphides. Synthesis of Triazoles. E. Fromm, L. Brück, R. Runkel, and E. Mayer (*Annalen*, 1924, **437**, 106—124).—A continuation of earlier work (cf. A., 1922, i, 377; Arndt and others, A., 1921, i, 813; 1922, i, 277, 375). 5-Amino-3-phenylamino-1 : 2 : 4-triazole has m. p. 163°, not 77° or 157°, as previously given. It forms a *benzylidene* compound, yellow needles, m. p. 225°, and a *tribenzoyl* derivative, yellow crystals, m. p. 126°. 3-Phenylamino-5-thiol-1 : 2 : 4-triazole may be oxidised to the corresponding disulphide which, treated with hot 25% sodium hydroxide, gives an equimolecular mixture (cf. *pp*′-dinitrodiphenyldisulphide, Fromm and Wittmann, A., 1908, i, 631) of the parent thioltriazole and 3-*phenylamino*-1 : 2 : 4-*triazole*, m. p. 180°, yielding a *dibenzoyl* derivative, m. p. 111—112°. 3-p-*Tolylamino*-5-*thiol*-1 : 2 : 4-*triazole*, from *p*-tolyldithiobiuret and hydrazine hydrate, forms colourless crystals, m. p. 271°; its *dibenzoyl* derivative, yellow leaflets, has m. p. 129°, and the *benzyl*(*thio*)*ether*, needles, m. p. 182°; this also yields a *benzoyl* derivative, scales, m. p. 133°. 5-*Amino*-3-p-*tolylamino*-1 : 2 : 4-*triazole*, the subsidiary product of the above reaction, has m. p. 178—180°, its *benzylidene* derivative, m. p. 219°. The thioltriazole, oxidised with ferric chloride, yields the *disulphide*, a yellow powder, m. p. 229°, which, treated with sodium hydroxide, gives, as above, 3-p-*tolylamino*-1 : 2 : 4-*triazole*, m. p. 199°, the

benzoyl derivative of which forms yellow leaflets, m. p. 172°. Similar compounds containing the *o*-tolyl and *o*-anisyl radicals were prepared. *Cyano-o-tolylcarbamide* has m. p. 65—68°; 3-o-*tolylamino*-5-*thiol*-1 : 2 : 4-*triazole* forms needles, m. p. 263°; its *dibenzoyl* derivative has m. p. 133°, the *benzyl(thio)ether*, m. p. 161°, and this also yields a *dibenzoyl* derivative, leaflets, m. p. 125°. 5-*Amino*-3-o-*tolylamino*-1 : 2 : 4-*triazole* has m. p. 165°, and easily decomposes; its *hydrochloride* forms needles, m. p. 187°, the *benzoyl* derivative, scales, m. p. 220°. o-*Tolylthiocarbamide* has m. p. 158°; the corresponding *triazole disulphide* forms a yellow powder, m. p. 277°. o-*Anisyldithiobiuret*, m. p. 148°, treated with iodine, gives o-*anisylthiuret hydriodide*, m. p. 200°, and with benzyl chloride a *compound*, m. p. 130°. 3-o-*Anisylamino*-5-*thiol*-1 : 2 : 4-*triazole* has m. p. 280°; its *benzyl(thio)ether*, m. p. 108°; its *dibenzoyl* derivative forms yellow scales, m. p. 138°. *Aminoguanidino-o-anisylthiocarbamide* crystallises in needles, m. p. 134—135°, its *hydrochloride* has m. p. 178—180°, and its *benzylidene* compound forms pale yellow scales. 5-*Amino*-3-p-*phenetylamino*-1 : 2 : 4-*triazole* has m. p. 191°, its *dibenzoyl* derivative, a yellow substance, melts at 176°, and its *diacetyl* derivative at 168°. 3-p-*Phenetylamino*-5-*thiol*-1 : 2 : 4-*triazole* has m. p. 268°, its *dibenzoyl* compound, m. p. 145°, its *benzyl(thio)ether* forms needles, m. p. 172°, and yields a *benzoyl* derivative, yellow needles, m. p. 122°. The corresponding *disulphide* is an amorphous powder convertible, as above, into 3-p-*phenetylamino*-1 : 2 : 4-*triazole*, m. p. 185°. 5-*Amino*-3-*ethylphenylamino*-1 : 2 : 4-*triazole* forms scales, m. p. 198°; its *benzoyl* derivative, yellow crystals, has m. p. 188·5°, its *acetyl* derivative m. p. 157°. The corresponding 5-*thioltriazole* forms needles, m. p. 127°, *dibenzoyl* derivative, m. p. 118°, *benzyl(thio)ether*, m. p. 94°, and the *benzoyl* derivative of the latter, m. p. 65°. The by-product of the hydrazine hydrate reaction here is 3-amino-5-thiol-1 : 2 : 4-triazole (cf. Fromm and Arndt, *loc. cit.*), ethylaniline being split off. This triazole yields a 1 : 4-*dibenzoyl* derivative, m. p. 178°. The *benzoyl* derivative of 5-*benzoylamido*-3-*thiol*-1 : 2 : 4-*triazole* has m. p. above 260°.

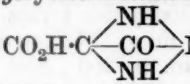
W. A. S.

Derivatives of *cyclo*Triazobutane [*cyclo*Triazomethene]. O. Diels and H. Behncke (*Ber.*, 1924, **57**, [*B*], 653—656).—The formation of additive products from azodicarboxylic ester and compounds containing an " acidic " methylene group is described (cf. A., 1923, i, 391, and previous abstracts).

Ethyl azodicarboxylate reacts with ethyl cyanoacetate in the presence of potassium acetate at 60° to form the *compound*, $CO_2Et{\cdot}C(CN){:}[N(CO_2Et){\cdot}NH{\cdot}CO_2Et]_2$, an unstable, yellow liquid, b. p. 150—155°/0·4 mm. Ethyl malonate reacts with ethyl azodicarboxylate to yield the *substance*, $(CO_2Et)_2C[N(CO_2Et){\cdot}NHCO_2Et]_2$, colourless, prismatic plates, m. p. 107°, which is remarkably stable towards acids and oxidising agents, and with methyl azodicarboxylate gives the corresponding *methyl* ester, m. p. 140—141°. Either ester is transformed by methyl-alcoholic potassium hydroxide solution into *potassium* cyclo*triazomethene*-1 : 3 : 4 : 4-*tetracarboxylate*,



which could not be freed completely from potassium carbonate, but is converted by acetic acid into *potassium hydrogen* cyclo*triazomethene*-4 : 4-*dicarboxylate*, pyramids, m. p. 287° (decomp.). The latter salt with sulphuric acid affords cyclo*triazomethene*-4 : 4-*dicarboxylic acid* (long prisms, m. p. 237°, after softening and decomposing at 218°), which passes in a vacuum at 100° into 2 : 4-*carbonyl*cyclo*triazomethene*-4-*carboxylic acid*,



The monocarboxylic acid loses carbon dioxide at 218°, to give 2 : 4-*carbonyl*cyclo*triazomethene*, colourless prisms, m. p. 237°.

H. W.

Action of Pyridine on Hydrazono-acid Chlorides. C. Bülow and F. Seidel (*Ber.*, 1924, **57**, [*B*], 629—633).—The compound [m. p. 186°, not 168°, as erroneously recorded by Bülow and Neber (A., 1913, i, 999)] obtained from 2 : 4-dichlorophenylhydrazinopyruvyl chloride and pyridine is shown to have the constitution, $CH_3{\cdot}CO{\cdot}C(C_5H_4N){:}N{\cdot}NH{\cdot}C_6H_3Cl_2$, since the basic properties of the pyridine nitrogen atom are retained in it, as is proved by the formation of a *hydrochloride*, m. p. 168°, a *chloroaurate*, and a *chloroplatinate*. Similarly, the pentabromo derivative obtained from 4-phenylazo-3-methylisoxazolone (Hecking, *Diss.*, Tübingen, 1913) or from ethyl phenylazoacetoacetate (Memminger, *Diss.*, Tübingen, 1910) is transformed by cold pyridine into the *compound*,

$$CH_3{\cdot}CO{\cdot}CH(C_5H_4N){\cdot}NBr{\cdot}NBr{\cdot}C_6H_3Br_2,$$

red needles, m. p. 162° (*hydrochloride*, m. p. 159—160°), which is converted by zinc and alcoholic hydrochloric acid into pyridine and *p*-bromoaniline. The composition $C_{15}H_{13}ON_3Br_4$ is assigned to the product of the action of pyridine on the pentabromo compound from 4-*o*-tolylazo-3-methylisoxazolone (Memminger, *loc. cit.*). The 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate is transformed by pyridine into the *substance* $C_{15}H_{14}O_2N_3Cl_3,H_2O$, yellow crystals, m. p. 142° after darkening at 130°. H. W.

Colour of Azo Compounds and their Salts. F. Kehrmann and S. Hempel (*Ber.*, 1924, **57**, [*B*], 751; cf. A., 1917, i, 593).—An acknowledgment of the priority of V. Piccard (A., 1913, i, 895), regarding the colours of 4 : 4′-diaminoazobenzene, its tetramethyl derivative, and their salts in different solvents. F. A. M.

Indoleazobenzene. W. Madelung (*Ber.*, 1924, **57**, [*B*], 751; cf. this vol., i, 423).—An acknowledgment of the preparation by Pieroni [*Atti R. Accad. Lincei*, 1921, (v), **30**, i, 267] of indoleazobenzene. F. A. M.

Preparation of Acylacetyl Compounds. Chem. Fabr. Griesheim-Elektron (Brit. Pat. 211814).—Acylacetyl compounds are obtained, under exactly similar conditions to those required in the preparation of diacylacetyl compounds (cf. Chem. Fabr.

Griesheim-Elektron, this vol., i, 671), by the interaction of an acylacetic ester and a monoamine of the general formula $NH_2{\cdot}R{\cdot}X{\cdot}R'$, where R represents an aryl residue, R′ the same or a different aryl residue or a heterocyclic or acyclic residue containing a methylene group capable of coupling with diazo compounds, X an azo or azoxy group, or the residue of a 5-membered heterocyclic nucleus. The products resemble the diacylacetyl compounds in their substantive character. The following compounds are described. *Acetoacetyldehydrothiotoluidine*: colourless, crystalline powder, m. p. 170—172° (decomp.); *acetoacetylbenzeneazo-1-naphthylamine*: slender, orange needles, m. p. 154—155° (decomp.); *acetoacetyl-4-aminoazobenzene*: yellowish-orange, finely-crystallised powder, m. p. 130—131°; *acetoacetyl-4′-aminobenzeneazo-1-phenyl-3-methyl-5-pyrazolone*: slender, orange-yellow, lustrous needles, decomp. 208°; *acetoacetyl-o-aminoazotoluene*: slender, orange-yellow needles, m. p. 147°; *acetoacetyl-m-aminoazotoluene*: orange, opalescent scales, m. p. 133—134°; *acetoacetyl-4′-chloro-4-aminoazobenzene*: slender, orange-yellow, felted needles, m. p. 188°; *acetoacetyl-3′-nitro-4-aminoazobenzene*: slender, orange-yellow, felted needles, m. p. 138° (decomp.); *acetoacetyl-4′-nitro-4-aminoazobenzene*: orange-red, lustrous scales, m. p. 190—191° (decomp.); *acetoacetyl-4-aminoazoxybenzene*: small, pale yellow rods, m. p. 138° (decomp.); *acetoacetyl-4′-amino-2′-methylbenzeneazo-2-naphthalene*: orange-yellow, spherical aggregates, m. p. 153—154°; *acetoacetyl-4′-aminobenzeneazo-p-cresol*: clusters of orange-yellow needles, m. p. 165°. W. T. K. B.

Dimorphism of Diphenylarsenious Chloride (Diphenylchloroarsine). C. S. Gibson and D. C. Vining (*J. Chem. Soc.*, 1924, **125**, 909—911).—Diphenylarsenious chloride (b. p. 178·6°/10 mm.) crystallises in two forms. The unstable modification, obtained by spontaneous crystallisation of freshly redistilled material, or by heating the stable form at 130° and cooling under "aseptic" conditions, forms needles, m. p. 18·2—18·4°, whilst the stable modification forms rhombic, biaxial crystals, m. p. 38·7—38·9°. [Cf. T., 1920, **117**, 777, 1447.] W. A. S.

Organo Derivatives of Bismuth. VII. Iodo and Nitro Derivatives of Triphenylbismuthine. J. F. Wilkinson and F. Challenger (*J. Chem. Soc.*, 1924, **125**, 854—864).—The red substance obtained by Challenger and Allpress (T., 1915, **107**, 17) consists mainly of phenyldi-iodobismuthine. *Triphenylbismuthine di-iodide*, Ph_3BiI_2, seems to be formed by direct union of triphenylbismuthine and iodine in ether solution at −78°, but decomposes at the ordinary temperature, giving the red solid. Triphenylbismuthine reacts with cyanogen bromide at 120°, giving diphenylbromobismuthine, bismuth oxybromide, and benzonitrile, whilst with cyanogen chloride scarcely any action takes place. This is in remarkable contrast to the action with cyanogen iodide (Challenger and Allpress, *loc. cit.*). Triphenylstibine and cyanogen iodide yield, presumably by interaction with moisture, in cold ether solution, *triphenylstibine hydroxyiodide*, $Ph_3Sb(OH)I$, m. p. 196°; tri-

phenylarsine and triphenylphosphine gave, with the same reagent, what appeared to be similar additive compounds which decomposed on contact with water (cf. Steinkopf and others, A., 1922, i, 72). A nitric–sulphuric acid mixture at −15°, or fuming nitric acid at its melting point, completely disrupts triphenylbismuthine, giving *m*-dinitrobenzene as the organic product; with benzoyl nitrate, however, a *dinitrate*, $Ph_3Bi(O{\cdot}NO_2)_2$, was obtained; *tri*-p-*chlorophenylbismuthine dinitrate*, m. p. 163—165°, was obtained in a similar way. Triphenylbismuthine dinitrate is converted by cold nitric acid (*d* 1·52), into, according to conditions, a *mononitro* derivative, convertible into an unstable *dichloride*, m. p. 105—110°; a *dinitro* derivative, yielding a *dichloride*, m. p. 136° (decomp.); a *tetranitro* derivative, convertible into the dichloride, m. p. 146°, which when heated until it decomposes gives *m*-chloronitrobenzene, the presumption being therefore that one nitro group in the bismuthine is in the meta-position (cf. Gillmeister, A., 1898, i, 138). *Tetranitrotriphenylbismuthine dihydroxide* was also obtained as an insoluble yellow powder, m. p. 108° (decomp.); boiled with alcohol it gives trinitrotriphenylbismuthine(?). Lastly, *hexanitrotriphenylbismuthine dinitrate* was obtained and converted into a *dichloride*, m. p. 148—149°. W. A. S.

Action of Inorganic Halides on Organo-metallic Compounds. F. Challenger and F. Pritchard (*J. Chem. Soc.*, 1924, **125**, 864—875).—A general discussion of earlier work (T., 1922, **121**, 104; cf. also Goddard and others, *ibid.*, 1923, **123**, 1163, etc.) and the following new observations. *Tri*-α-*naphthylstibine*, m. p. 218°, from antimony trichloride and magnesium α-naphthyl bromide, gives a *dichloride*, m. p. 260°, and a yellow *dibromide*, m. p. 229° (decomp.). *Tri*-m-*tolylbismuthine dibromide* has m. p. 92°. Although tri-*m*-tolylarsine may be obtained in a similar way from the appropriate Grignard reagent, *tri*-m-*tolyl stibine hydroxychloride*, m. p. 209°, was the only product obtained by treating antimony trichloride with magnesium *m*-tolyl bromide. Triphenylstibine and phosphorus trichloride interact in the cold to give mainly triphenylstibine dichloride; triphenylarsine only reacts with the same reagent at 160°, and then incompletely, yielding diphenylchloroarsine; triphenylphosphine gives the dichloride and decomposition products. Arsenic trichloride and triphenylstibine at 80° yield triphenylstibine dichloride and a little arsenic. Antimony trichloride and triphenylarsine form an additive *compound*, m. p. 78°. The same reagent with triphenylphosphine produces a similar *compound*, m. p. 96°. Triphenylphosphine forms analogous compounds with arsenic trichloride [product has m. p. about 100° (decomp.) and a little arsenic separated] and with bismuth chloride (m. p. 100—105°). The latter, heated at 270° and treated with water, gave metallic bismuth and triphenylphosphine oxide. Triphenylbismuthine and stannic chloride also form an additive compound. Triphenyl-bismuthine and -stibine react to some extent with silicon tetrachloride, giving diphenylchlorobismuthine and triphenylstibine dichloride, respectively; triphenylarsine does

not react. Titanium tetrachloride and triphenylbismuthine form a red compound and eventually yield diphenylchlorobismuthine; triphenylstibine gives only the dichloride, whilst triphenylarsine gives an unstable additive product. Attempts to prepare organic titanium compounds by interaction of titanium tetrachloride and magnesium phenyl bromide failed. W. A. S.

Fractionation of Gelatin by Extraction with Alcohol and Precipitation with Aluminium Hydroxide and Barium Chloride. M. A. RAKUSIN (*Chem.-Ztg.*, 1924, **48**, 249—250).—A sample of commercial "*Gelatina albissima*" was extracted with 95% alcohol, and the extract and the residue were investigated by precipitation with 10% aluminium hydroxide, the filtrate being precipitated with barium chloride. The various fractions were tested by the biuret, Ostromisslenski, and Molisch reactions, and and the composition of the gelatin is given as follows: free amino compounds, 0·50%; free carbohydrates, 0·96%; biuret complex, 49·27%; combined carbohydrates, 23·77%; combined chondroitin–sulphuric acid, 25·50%. The distribution of the mineral matter (3·29%) is uncertain. All the sulphur present in gelatin is combined in the form of chondroitin–sulphuric acid, which contains 5·71% of sulphur. Gelatin is therefore not an individual chemical substance, and gelatins obtained from different raw materials may have different properties. H. C. R.

Gelatin-sulphuric Acid and Casein-sulphuric Acid. J. HATANO (*Biochem. Z.*, 1924, **145**, 182—185).—By the action on gelatin and casein, in the presence of pyridine, of chlorosulphonic acid dissolved in dry chloroform, stable sulphates of these proteins are obtained. The preparation of gelatin sulphate obtained contained 1·7% of sulphur against 0·35% in the original gelatin, whilst casein sulphate preparations contained 0·84% and 1·38% of sulphur as compared with 0·62% in the original protein. J. P.

Products of Prolonged Tryptic Digestion of Casein. S. FRÄNKEL, H. GALLIA, A. LIEBSTER, and S. ROSEN (*Biochem. Z.*, 1924, **145**, 225—241).—After prolonged hydrolysis (2 months) of casein, the following products have been isolated: *d*-tyrosine anhydride, *d*-tryptophan anhydride, *d*-leucine anhydride, and histidine anhydride. The first three dextrorotatory anhydrides are supposed to arise from the lævorotatory amino-acids by the successive actions of the enzymes waldenase—bringing about an optical inversion—and anhydrase. In addition *d*-alanine, *d*-glutamic acid, *l*-oxyproline, *l*-serine, and *d*-valine were obtained, in part as such, and in part as the racemic forms. *l*-Proline, $[\alpha]_D^{12}$ −74·08° in water, *d-iso*leucine, $[\alpha]_D^{12}$ +12·77° in water, and *l*-aspartic acid were isolated in the unchanged condition, whilst glycine was partly converted into methylamine by the action of a decarboxylase. In the course of such prolonged hydrolysis, leucine is converted into the anhydride whilst *iso*leucine remains unchanged (cf. also A., 1922, i, 184; 1923, i, 398). J. P.

Protein Coagulation in Drops. IV. Influence of the Nature of the Proteins and Precipitants on the Precipitate. L. Cikánek, J. Havlík, and F. Kubánek (*Biochem. Z.*, 1924, **145**, 98—103).—The influence of a large number of substances on the coagulation of serum proteins has been studied, using the Bečka drop method. The presence in the precipitant of halogens, hydroxyl, sulphonyl, and nitro groups increases the precipitating action, whilst amino groups lower it. The precipitating powers of the aliphatic alcohols decrease with increase in the number of hydroxyl groups. With certain solutions of sodium sulphide, potassium hydroxide, and potassium cyanide, the albumin, but not the globulin, fraction is precipitated, whilst the reverse result is obtained with solutions of copper sulphate, cadmium nitrate, aluminium chloride, and disodium hydrogen phosphate. Certain pathological horse sera show a characteristic behaviour on precipitation with ferrous sulphate, pyrogallol, and tannin. J. P.

Influence of Hydrolysis on the Capacity of Proteins to Bind Acids and Bases. T. B. Robertson (*Austral. J. Exp. Biol.*, 1924, **1**, 31—37).—The ratio, equivalents of acid or base bound/equivalents of free amino-nitrogen, has been determined for casein and gelatin before and after hydrolysis by trypsin at p_H 2·0, 8·2, and 10·5. Except for gelatin at p_H 10·5, the ratio decreases as a result of hydrolysis. It is concluded, therefore, that the predominant method of union of proteins with acids and bases is through internal –CO·NH– groups rather than through free amino or carbonyl groups. O. O.

Halogenated Proteins. I. Bromo-ovalbumin. A. J. J. Vandevelde (*Rec. trav. chim.*, 1924, **43**, 158—162).—The action of bromine dissolved in carbon tetrachloride on some proteins in the form of a dry powder afforded bromo derivatives of higher halogen content than previously recorded. This is stated to be due to the fact that secondary reactions brought about by the presence of water were obviated. The following bromo derivatives (hygroscopic, orange-coloured powders of penetrating odour) are described: *Bromo-ovoprotein A*, soluble in water, yielding a strongly acid solution in which 87·1% of the total bromine is in the form of hydrobromic acid. At 100°, the substance loses hydrogen bromide to give *bromo-ovoprotein C*, which also yields an acid solution. Its colour, however, prevents it being examined with a coloured indicator. On dissolving the first-named substance in *N*-sodium hydroxide and then acidifying with acetic acid, a precipitate of *bromo-ovoprotein S* is formed. The percentages of bromine in these three substances are 37·5, 31·48, and 4·73, respectively. H. J. E.

Protein Phytotoxins, with Special Reference to the New "Modeccin." H. H. Green and P. Kamerman (*J. S. Afr. Chem. Inst.*, 1924, **7**, 3—5).—The roots of *Modecca digitata* (more correctly, *Adenia digitata*) contain a highly poisonous phytotoxin to which the name *modeccin* has been given; the fatal dose is

0·0005 mg. per kg. of body-weight, when injected intravenously or subcutaneously. In its general properties the substance resembles the other known phytotoxins, namely, ricin (from *Ricinus communis*), abrin (from *Abrus precatorius*), crotin (from *Croton tiglium*), robin (from *Robinia pseudacacia*), and curcin (from *Jatropha curcus*); all are stable up to about 70°, but destroyed rapidly at 100°. They are insoluble in 60% alcohol and are precipitated by ammonium sulphate and other salts. Modeccin resists hydrolysis by pepsin or trypsin for 3 days at 37°, but is destroyed by trypsin in 14 days; it does not possess hæmagglutinative properties and in this respect differs from ricin. W. P. S.

Protein Studies. III. Decomposition of Silk Fibroin by Fermentation. F. Wessely.—(See i, 696.)

Biochemistry.

Effect of Salts of Calcium, Sodium, and Potassium on Respiratory Exchanges. I. Effect of Parenteral Administration of these Salts. W. Arnoldi and J. Ferber (*Z. klin. Med.*, 1923, **97**, 208—216; from *Chem. Zentr.*, 1924, i, 494).—Injection of salts of calcium, sodium, and potassium produced increased utilisation of oxygen and diminution in respiratory quotient and the output of carbon dioxide in humans. Respiration within the tissues was increased. G. W. R.

Catalytic Action of Blood. L. Walling and O. O. Stoland (*Amer. J. Physiol.*, 1923, **66**, 503—518).—Blood catalase is accurately determined by reaction at p_H 8·9, 22°, for 0·5 hour; it is destroyed above 47° and is only slightly affected at 0°. In acid hydrogen peroxide at 22° it is apparently destroyed and its action complete in 10 minutes; with optimum alkalinity it acts for 3 hours or more. Sodium chloride (0·9%) in acid hydrogen peroxide increases, and in alkaline retards, the catalytic effect of blood. Chemical Abstracts.

Influence of Rarefied Air on the Gaseous Metabolism of the Blood. A. Loewy and J. Förster (*Biochem. Z.*, 1924, **145**, 318—323).—The blood of rabbits which had been kept under diminished pressure (430—460 mm.) for 24 to 33 hours showed a greater oxygen consumption than that of normal rabbits. The average figures found per 100 c.c. of blood per hour were 5·272 c.c. in the former and 2·733 c.c. in the latter case. J. P.

Cell Volume and Electrical Conductivity of Blood. H. C. Gram (*J. Biol. Chem.*, 1924, **59**, 33—40).—The conductivity of whole blood and of serum, and the cell volume, were measured. An empirical curve has been obtained from which the cell volume

may be read, if the ratio of the conductivity of the whole blood to that of the serum is known. W. O. K.

Rarefied Air and Blood Regeneration by "Hæmopoietins." J. FÖRSTER (*Biochem. Z.*, 1924, **145**, 309—317).—Serum from rabbits which had been kept in atmospheres at a pressure of 410 to 480 mm. for 1—2 days injected into rabbits rendered anæmic by bleeding, produced an increase in the rate at which the number of the red blood-corpuscles returned to the normal value. Normal sera and the proteins of milk did not produce this effect, which is ascribed to the production in the bone marrow, under the stimulus of the diminished pressure, of active substances—"hæmopoietins" (Carnot and Deflandre, *Compt. rend.*, 1906, **143**, 384)—which then find their way into the blood-stream. J. P.

Ultrafiltration of Blood Serum and Cerebrospinal Fluid. G. EGERER-SEHAM (*J. Lab. Clin. Med.*, 1923, **8**, 818—824).—A new apparatus is described. The ammonium sulphate globulin test is negative in the majority of ultrafiltrates of normal blood serum. The ultrafiltrates of non-syphilitic and syphilitic blood give a reduction of the colloidal gold solution in almost all cases. The ultrafiltrates of normal cerebrospinal fluid give no colloidal gold curve. The reduction of colloidal gold solution by ultrafiltrates from syphilitic spinal fluids seems to vary with the quantity of the substance reducing the colloidal gold solution present in the original spinal fluid. The substance giving the Wassermann reaction in syphilitic blood does not seem to be ultrafiltrable. CHEMICAL ABSTRACTS.

Calcium-ion Concentration of Blood Plasma. E. J. BIGWOOD (*Bull. Soc. Chim. biol.*, 1924, **6**, 118—141).—In 20 normal subjects the calcium-ion concentration varied from 22 to 28 mg. per litre of venous blood plasma. The individual variations in any one subject are closely parallel to the variations in p_H, increasing with increasing acidity and *vice versâ*. Such a parallelism does not exist between the calcium-ion and bicarbonate-ion concentrations. J. P.

Effect of Fasting (and Re-feeding) on the Calcium and Inorganic Phosphorus in Blood Serums of Normal and Rachitic Rats. A. W. CAVINS (*J. Biol. Chem.*, 1924, **59**, 237—242).—After fasting, the subnormal quantities of inorganic phosphorus present in the serum of rachitic rats increased approximately to normal, and the rickets healed concurrently. In the case of normal rats, there was no similar rise in the inorganic phosphorus in the serum after fasting. W. O. K.

Dynamics of Phosphoric Acid in the Blood. H. LAWACZECK (*Biochem. Z.*, 1924, **145**, 351—371).—The free phosphoric acid of whole blood was found to vary between 7·8 and 18·2 mg.%. When the blood was kept at or below body temperature part of the inorganic was converted into organic phosphate and this con-

version was increased by the passage of air or hydrogen through the blood, but it did not occur if the blood had been previously warmed at 44—45°. The reverse conversion of organic into inorganic phosphate resulted from passing carbon dioxide. The reversible interconversion: inorganic $\rightleftharpoons$ organic phosphate was found to proceed towards the right in the presence of phosphates, bicarbonate, and calcium, and towards the left in the presence of chlorides, water (hæmolysis), potassium, and sodium, but the cations mentioned were active only in hæmolysed blood. Both inorganic and organic phosphorus compounds passed from the serum into the corpuscles, and *vice versâ*.

The phosphates taking part in the above changes are acid-soluble, but hexosephosphate, which appears to be a product of the synthetic phase of the reaction, is not subject to the reverse hydrolytic change. J. P.

Proteins of Immune Sera, especially the Ratio of Globulin to Albumin (Protein Index). S. Bächer and M. M. Kosian (*Biochem. Z.*, 1924, **145**, 324—343).—An investigation of the amounts of protein precipitable from various normal and immune sera by one-third and one-half saturation with ammonium sulphate. Wide differences exist in the values obtained from the same types of sera from different animals, whilst old sera have a higher protein index than fresh sera and are thus regarded as more labile. Diphtheria sera (horse) show a higher total protein content than the normal, and absolute and relative increases in globulin, notably in pseudoglobulin, and decreases in albumin. During immunisation the lability of horse sera progressively increases, but this is not directly related to the formation of antitoxin. Immunisation of the horse against toxins other than diphtheria does not produce analogous results, nor does diphtheria toxin produce the same effects when injected into oxen. The increased lability of the proteins of old sera is associated with a similar alteration in the ease with which the antitoxin may be salted out with ammonium sulphate. J. P.

Action of Thrombin. IX. Blood Clotting. E. Wöhlisch (*Biochem. Z.*, 1924, **145**, 279—285).—The observation of Stuber and Sano (A., 1923, i, 410) that thrombin prepared by Schmidt's method, when separated from a solution of fibrinogen by a semi-permeable membrane, causes the fibrinogen to clot, was not confirmed when proper controls were employed. The views of these authors (*loc. cit.*) regarding the difference between the thrombin of fresh serum and that precipitated by alcohol according to Schmidt's process are not supported. J. P.

Nature of the Antihæmolytic Property of Heated Sera. G. Milkovitch (*Compt. rend. Soc. Biol.*, 1923, **89**, 877—879; from *Chem. Zentr.*, 1924, i, 356).—Hæmolysis is conditioned, not simply by the presence of a hæmolytic agent, but also by certain chemical factors, in particular the reaction, which must be to a certain degree alkaline. From experiments with human sera heated at

56° it is concluded that the presence of a specific "antihæmolysin" is improbable and that heating simply results in the production of chemical conditions unfavourable to hæmolysis. G. W. R.

Coagglutinating and Precipitating Action of Ricin. G. DI MACCO (*Z. Immunit.*, 1923, **38**, I, 467—488; from *Chem. Zentr.*, 1924, i, 493—494).—In addition to the direct agglutinative effect of ricin on certain blood-corpuscles, agglutination with corpuscles on which it cannot by itself exert any action, can be produced in the presence of serum from other animals. This coagglutination is not shown when ricin is first allowed to react with the serum in the absence of blood-corpuscles. Coagglutination is related to the precipitating action of ricin; it is considered to be physico-chemical in nature. G. W. R.

Precipitin Reactions of a Crystalline Globulin from Human Urine. H. S. EVERETT, S. BAYNE-JONES, and D. W. WILSON.—(See ii, 432.)

Potassium Fluoride as Preservative for Blood. R. H. MAJOR (*J. Amer. Med. Assoc.*, 1923, **81**, 1952).—In the absence of bacteria, clotting is prevented, and the sugar and carbon dioxide tension are unchanged during 7 days when potassium fluoride is added to blood. CHEMICAL ABSTRACTS.

Use of Formaldehyde for the Preservation of Blood Specimens. J. C. BOCK (*J. Biol. Chem.*, 1924, **59**, 73—76; cf. *ibid.*, 1920, **44**, 203).—The use of formaldehyde for preservation of blood for determinations of sugar by the method of Folin and Wu is inadvisable, as five of the six samples of formalin tested gave rise to markedly high results. W. O. K.

Animal Calorimetry. XXIV. Oxidation of Mixtures of Carbohydrates and Fat. A Correction. G. LUSK (*J. Biol. Chem.*, 1924, **59**, 41—42).—Corrections are given of errors in the standard table of Luntze and Schumberg ("Studien zu einer Physiologie des Marsches," Berlin, 1901, 361), showing the caloric value of 1 litre of oxygen used to oxidise mixtures of carbohydrates and fats. W. O. K.

Clinical Calorimetry. XXXV. A Graphical Representation of the Respiratory Quotient and the Percentage of Calories from Protein, Fat, and Carbohydrate. E. F. DU BOIS (*J. Biol. Chem.*, 1924, **59**, 43—49).—Graphs have been constructed from which it is possible to determine rapidly the number of calories produced by each litre of oxygen, knowing the total respiratory quotient and the percentage of calories furnished by protein. W. O. K.

Clinical Calorimetry. XXXVI. A Graphic Method of Determining certain Numerical Factors in Metabolism. A. M. MICHAELIS (*J. Biol. Chem.*, 1924, **59**, 51—58).—A graph is given from which it is possible to determine easily the total calories

produced when 1 litre of oxygen is used in the combustion of a mixture of fats, proteins, and carbohydrates, from a knowledge of the urinary nitrogen, the total oxygen consumed, and the total respiratory quotient. From another graph, the percentage of calories derived from protein, fat, and carbohydrate, and that of oxygen used in the oxidation of each, may be read. W. O. K.

Thermochemistry of Protein Behaviour. J. H. Mathews and B. W. Rowland (*Colloid Symposium Monograph, Univ. Wisconsin*, 1923, 227—243).—Fixed amounts of 0·5*N*-hydrochloric acid were added to gelatin solutions of varying concentrations at 40° and the thermal change was recorded in Browne's adiabatic calorimeter. When in concentration greater than about 2%, gelatin containing 1·3% of ash shows markedly different results from ash-free isoelectric gelatin. Collateral experiments are described with gelatin and glycine. Chemical Abstracts.

Formation in the Injured Liver of a Compound Similar to Dextrose but Unsuitable for the Organism. Varela and Rubino (*Arch. exp. Path. Pharm.*, 1924, **101**, 316—334).—The occurrence of hypoglycæmia or of abnormally low hyperglycæmia after the oral administration of 10—20 g. of dextrose or lævulose is taken as an indication of the presence of a sugar unsuitable for utilisation. In certain diseases of the liver, this appears to obtain. It is suggested that the formation of glycogen does not involve merely the polymerisation of dextrose, but that there is a complex assimilation process. W. O. K.

Stimulus of Food on Intermediary Metabolic Processes. I. W. Laufberger and J. A. Šefčík (*Biochem. Z.*, 1924, **145**, 274—278).—The oral administration of peptone or egg-albumin to rabbits produced a hyperglycæmia within 5 minutes. Mechanical stimulation of the gastric mucous membrane or the administration of olive oil had no influence on the blood-sugar. J. P.

Preparation of Insulin. N. F. Fischer (*Amer. J. Physiol.*, 1923, **67**, 57—64).—The method of Doisy, Somogyi, and Shaffer (*J. Biol. Chem.*, 1923, **55**, xxi) is modified by effecting the final precipitation in two stages, with 1 and 8 volumes of alcohol, respectively. The first fraction is toxic, and produces a rise in the blood-sugar; the second is active, and of a potency which is the greater the smaller the amount of toxic substance present. Pancreas from old cows yielded only 100 units of insulin per kg., whilst that from calves yielded 1000 units. A. A. E.

Insulin-like Substance in the Kidney, Spleen, and Skeletal Muscle. J. S. Ashby (*Amer. J. Physiol.*, 1923, **67**, 77—82).—A substance extracted from the kidney, spleen, and muscle of normal dogs and cattle, after the removal of the "toxic fraction," behaved similarly to insulin in producing hypoglycæmia in rabbits. Hypoglycæmia produced by the kidney extract was maintained for the unusually long period of at least 24 hours. A. A. E.

Amount of Available Insulin in the Pancreas of Domestic Animals. F. FENGER and R. S. WILSON (*J. Biol. Chem.*, 1924, **59**, 83—90).—The average yield of insulin from 1 kg. of fresh pancreas of cattle, sheep, or pig was from 1500 to 2200 rabbit units. The methods of purification and standardisation of the insulin are described in detail. W. O. K.

Disposal of Fat in the Organism. F. KÖSZEG (*Arch. exp. Path. Pharm.*, 1924, **101**, 305—315).—Iodipin (Merck), a fat containing iodine, was introduced in an emulsified form into the jugular vein of a dog. The quantities of iodine, up to about 2% of the weight of tissue, accumulated in the lung, were larger than was found in the liver or spleen. These results lend support to the view that the lung is active in the removal of fat from the blood-stream. W. O. K.

Autolysis. X. The Autolysis of Muscle. K. K. CHEN and H. C. BRADLEY (*J. Biol. Chem.*, 1924, **59**, 151—164).—The rate of autolysis of the muscles of warm-blooded animals, as measured by the production of amino-acids not precipitated by trichloroacetic acid, is at a maximum at p_H 4·5—5·0. This agrees with the fact that *in vivo* atrophy of muscle-tissues follows conditions leading to an acidosis in the muscle-cells. In warm-blooded animals, there appears to be a relation between the activity and pigmentation of the muscle and the degree of autolysis, and similarly in the case of fish-muscle, the degree of autolysis appears to be determined by the activity of the muscles. In the molluscs examined, autolysis is slight and practically unaffected by reaction. W. O. K.

Amino-acids in Nutrition. VI. Nature of the Supplementary Value of Protein-free Milk to the Total Proteins of the Milk. VII. Cause of Nutritive Inadequacy of the Proteins of the Georgia Velvet Bean (*Stizolobium Deeringianum*). B. SURE (*J. Metabolic Res.*, 1923, **3**, 373—382, 383—391).—VI. The effect is attributed to cystine or some other organic sulphur compound which may be transformed into cystine, and to traces of tyrosine in addition.

VII. The inadequacy is due to indigestibility and to deficiency of amino-acids, the latter being remedied by the addition to the diet of casein and cystine. CHEMICAL ABSTRACTS.

Metabolism of Sulphur. VI. Oxidation of Cystine in the Animal Organism. II. H. B. LEWIS, H. UPDEGRAFF, and D. A. MCGINTY (*J. Biol. Chem.*, 1924, **59**, 59—71).—The sulphur in dibenzoylcystine which has been subcutaneously injected into rabbits is not oxidised, but as in the case of phenyluraminocystine (Lewis and McGinty, *ibid.*, 1922, **50**, 303; **53**, 349) it is partly reduced to form the sulphydryl group before excretion in the urine. When dibenzoylcystine is administered orally, a part of the sulphur is oxidised, but this is probably because the compound is partly hydrolysed into benzoic acid and cystine in the alimentary canal. W. O. K.

Substitution of Taurine for Cystine in the Diet of Mice. M. L. MITCHELL (*Austral. J. Exp. Biol.*, 1924, **1**, 5—9).—That taurine can replace cystine to a considerable extent is suggested by the fact that the addition of either to a cystine-deficient diet produces growth which does not take place otherwise, and ceases immediately the taurine or the cystine is removed. O. O.

Metabolism of Benzoic Acid in the Human Organism. J. NEUBERG (*Biochem. Z.*, 1924, **145**, 249—273).—After the administration of 10 to 15 grams of sodium benzoate to human subjects with normal or impaired kidney functions, no free benzoic acid was found in the urine. The sodium benzoate appears in the urine, not only as hippuric acid (90%), but also as (possibly) benzoylglycuronic acid (10%). It is concluded that methods of determining hippuric acid based on the determination of the benzoic acid freed by hydrolysis give results which are too high. J. P.

Nutrition and Growth on Diets Highly Deficient or Entirely Lacking in Preformed Carbohydrates. T. B. OSBORNE and L. B. MENDEL [with H. C. CANNON] (*J. Biol. Chem.*, 1924, **59**, 13—32).—Rats fed on a diet composed of protein, with varying proportions of fat, inorganic salts, and some source of vitamins, but containing no preformed carbohydrates, showed in many instances good growth, although, as a rule, the male rats did not attain weights greater than about 250 g. W. O. K.

Vitamin Potency of Cod-liver Oil. A. D. HOLMES (*J. Metabolic Res.*, 1923, **3**, 393; cf. *ibid.*, 1922, **2**, 113, 361).—The liver oil of emaciated cod caught in March has not so high a vitamin-*A* potency as that from well-nourished fish caught in later seasons. CHEMICAL ABSTRACTS.

Experimental Rickets. XXIV. Effect of certain Extracts of Plant Tissues on Florid Rickets. P. G. SHIPLEY, E. M. KINNEY, and E. V. MCCOLLUM (*J. Biol. Chem.*, 1924, **59**, 165—175).—Ether, alcohol, and water extract from lucerne leaves a substance which cures rickets in rats. Lucerne, extracted by ether, does not induce healing. Ether extracts an antirachitic vitamin from clover blossom, but, on the other hand, extracts of dry spinach, Brussels sprouts, cabbage, celery, tomato, and sweet potato were without antirachitic effect. W. O. K.

Experimental Rickets. XXV. Antirachitic Effect of certain Oils. P. G. SHIPLEY, E. M. KINNEY, and E. V. MCCOLLUM (*J. Biol. Chem.*, 1924, **59**, 177—182).—The following oils have no antirachitic effect: oil of sandalwood, oil of lemon, oil of orange-peel, oil of palm, fraction of butter fat insoluble in alcohol, Japan wax, oil of spice, oil of fennel seed, spermaceti, and sperm oil. Oil of cloves and the alcoholic extract of butter fat contain antirachitic vitamin. W. O. K.

Value of Bezssonoff's Reaction for indicating the Presence of Vitamin-*C* in the Juice of Sauerkraut. P. E. WEDGWOOD and F. L. FORD (*Bull. Soc. Chim. biol.*, 1924, **6**, 217).—A sample

of the juice of sauerkraut which gave a blue coloration with Bezssonoff's reagent (*ibid.*, 1923, **4**, 83) failed to protect guinea-pigs from scurvy. It is concluded that Bezssonoff's reagent is not an infallible indicator of vitamin-*C*. C. T. G.

Additional Requirement for the Test with the Reagent for Vitamin-*C*. N. Bezssonoff (*Bull. Soc. Chim. biol.*, 1924, **6**, 220).—A reply to Wedgwood and Ford (see preceding abstract). A blue coloration indicates the presence of vitamin-*C* only if the colour is intensified on heating the liquid for a short time. If the colour is reduced or disappears on heating, vitamin-*C* is absent. The maximum dose used by Wedgwood and Ford in their experiments on guinea-pigs is considered to be too small to prove that vitamin-*C* is absent. C. T. G.

Persistence of Vitamin-*C* in the Livers of Rats on a Scorbutic Ration. S. Lepkovsky and M. T. Nelson (*J. Biol. Chem.*, 1924, **59**, 91—96).—The livers of rats fed from soon after the time of weaning on a ration as far as possible free from vitamin-*C* contain marked quantities of this vitamin as shown by the effect on the growth of guinea-pigs fed on a diet free from vitamin-*C*. A second generation of rats also fed on a diet free from vitamin-*C* likewise showed no diminution of this vitamin in the liver. W. O. K.

Importance of Zinc on the Nutrition of Animals. Experiments on Mice. Bertrand and Benzon (*Bull. Soc. Chim. biol.*, 1924, **6**, 203).—It was found impossible to remove all traces of zinc from natural food materials without also removing vitamin-*B*, with which the zinc appeared to be associated. A synthetic food, based on the composition of wheat, was therefore used. Mice receiving the synthetic food with the addition of an amount of zinc as sulphate equivalent to that present in a normal diet of wheat lived 25—50% longer than those receiving the synthetic food alone. In the absence of any supply of zinc in the food, the amount present at the beginning is retained throughout life, whilst, if zinc be given, the original amount present is about doubled. C. T. G.

Non-reciprocal Permeability. III. Non-reciprocal Permeability of Ions and of Colouring Matters. E. Wertheimer (*Pflüger's Archiv*, 1923, **200**, 354—365; from *Chem. Zentr.*, 1924, i, 346; cf. *Pflüger's Archiv*, 1923, **200**, 82).—The non-reciprocal permeability shown by the cuticular membrane of frogs is confined to sodium ions. Other cations pass equally freely in both directions. Anions are without influence. Colouring matters behave differently according as they are acidic or basic, the former passing the membrane in an inward direction and the latter in an outward direction. Some acidic and basic colouring matters can pass in either direction. The phenomena are influenced by the reactions on the inner and outer side of the membrane. By making use of non-reciprocal permeability, mixtures of colouring matters may be separated. G. W. R.

Radioactivity of Living Cells. A. NODON (*Compt. rend.*, 1924, **178**, 1101—1102).—The radioactivity of living cells has been demonstrated by photographic means. A sample of barium–radium sulphate, a living insect (*Pœcicoloris*), and a green leaf were confined separately in boxes so as to be able to affect a photographic plate, without coming into contact with the sensitive surface. After 20 hours' exposure, the radium salt gave a strong impression, the insect a more feeble impression, and the leaf a thin film. The activity indicated is of the same order as that indicated by electrometric measurements. [Cf. this vol., i, 347.]

A. B. H.

Coagulation and Structure of the Egg. J. AMAR (*Compt. rend.*, 1924, **178**, 803—805; cf. this vol., ii, 144).—Desiccation of birds' eggs over sulphuric acid showed that egg-white and egg-yolk contain 86% and 48% of water, respectively. Desiccation and re-hydration are completely reversible, unless structural changes (such as are caused by heating or by alcohol) intervene. The dried white contains spiraloid forms (insoluble albumin) in a homogeneous mass (soluble albumin). Sodium chloride does not cause the coagulation of the white or the yolk. The chlorides of potassium, magnesium, calcium, barium, and zinc effect coagulation to an increasing amount (in the order given). Sodium phosphate (present in the egg) hinders coagulation.

E. E. T.

Sugar in the Cerebrospinal Fluid. G. H. MOATES and J. J. KEEGAN (*J. Lab. Clin. Med.*, 1923, **8**, 825—828).—The normal range of cerebrospinal fluid sugar is 0·040—0·068%. The concentration is increased in most cases of epidemic encephalitis but decreased in infectious meningitis. There is no apparent relation between the sugar content of the cerebrospinal fluid and the Wassermann reaction, colloidal gold curve, cell count, globulin, or total protein.

CHEMICAL ABSTRACTS.

Bile Secretions. IV. Colorimetric Determination of Bile Acids in Human Body Fluids. F. ROSENTHAL and F. LAUTERBACH.—(See ii, 431.)

Mechanism of Muscular Action. O. W. TIEGS (*Austral. J. Exp. Biol.*, 1924, **1**, 11—29).—It is considered that lactic acid is liberated from only one of the excitable membranes, and at the same time the other membrane must liberate a basic substance, hitherto unrecognised. When this happens, the processes constituting a muscle twitch must occur and their nature can be explained on a physico-chemical basis.

O. O.

Alteration of the Constituents of Preserved Flesh. I. A. SMORODINZEV and A. N. ADOWA (*Z. physiol. Chem.*, 1924, **135**, 41—48).—Large quantities of salt solution were pumped into the aorta shortly after killing, and the extractive substances in the muscle-tissues examined after storage for 15 months. The creatinine content was the same as that of fresh flesh, whilst the creatine was

reduced to one-fifth or one-tenth. The fact that there was no increase in the amount of methylguanidine suggests that this compound does exist in the tissues and is not necessarily the product of an oxidation occurring during the extraction of creatinine (cf. Ewins, A., 1916, i, 528). E. M. C.

Oxidising Power of the Nuclei of the Epithelium of the Renal Canaliculi of *Perca fluviatilis*. M. Manquat (*Compt. rend.*, 1924, **178**, 972—974).—The nuclei of the epithelial cells of the renal canaliculi of the perch appear to possess oxidising properties, since they become blue when indigo-carmine is injected into the alimentary canal, whereas the cytoplasm remains colourless. This phenomenon was not observed with any of the other species of fresh-water fish examined. T. H. P.

Venom of *Lachesis ammodytoides*. B. A. Houssay and J. Negrete (*Compt. rend. Soc. Biol.*, 1923, **89**, 751—753; from *Chem. Zentr.*, 1924, i, 491).—The venom of this Argentine snake is golden-yellow and contains 34—40% of water. It precipitates the anti-serum for *Lachesis alternatus*, but only slightly that for *Crotalus terrificus*. It has no amylolytic effect and does not attack neutral fats. A description of its physiological effects is given. G. W. R.

Excretion of Creatinine by the Kidneys. V. Cantinieaux (*Compt. rend. Soc. Biol.*, 1923, **89**, 848—851; from *Chem. Zentr.*, 1924, i, 358).—The amount of creatinine eliminated in the urine of healthy men is a function of the total creatinine (preformed creatinine + creatine) in the blood. The relationship is expressed according to Ambard's formula by the constant 0·07 for normal individuals. In cases of depressed renal activity there is a parallelism with the constant for urea. The formulæ of Austin, of Stillman, and of Van Slyke give similar results. No constant results are given when the amount of preformed creatinine in the blood alone is used in the above formulæ. G. W. R.

Electropy. VII. Excretion of Electropic Dyestuffs and Carbinols. L. Karczag and L. Paunz (*Biochem. Z.*, 1924, **145**, 345—350).—Electropic dyestuffs of the triphenylmethane group administered subcutaneously or intravenously to rabbits or guinea-pigs were found in the urine, bile, cerebrospinal fluid, aqueous humour of the eye, peritoneal exudate, and amniotic fluid as colourless carbinols. The less the dispersion of the dyestuff the more slowly is it excreted; the most highly dispersed dyestuffs are excreted by the kidney whilst less highly dispersed dyes are found in the bile. The electrostatic charge on the particles of the dyestuffs is of importance in their conversion and excretion. J. P.

Porphyrin Formation. I. O. Schumm (*Z. physiol. Chem.*, 1924, **133**, 308—320).—The increase in the porphyrin content of the fæces, associated with diet (A., 1923, i, 732), is considered as originating from a constituent of the flesh. The porphyrin prepared from rotting flesh has been examined spectroscopically; it

differs from coproporphyrin, but appears to resemble closely the porphyrin prepared from blood by the author, and also that described by Kämmerer and Fischer (cf. Fischer and Schneller, A., 1923, i, 1244). Coproporphyrin could not be found in fresh beef or in frozen meat. O. O.

Correction of "Natural Porphyrins." III. O. Schumm (*Z. physiol. Chem.*, 1924, **133**, 298—307; cf. Fischer and Schneller, A., 1923, i, 1244).—Mainly polemical. The author claims priority in this work, and sees no reason to change the views put forward in his previous paper (A., 1923, i, 631). O. O.

Menstruation and the Choline Balance. E. Sieburg and W. Patzschke (*Z. ges. exp. Med.*, 1923, **36**, 324—343; from *Chem. Zentr.*, 1924, i, 572).—The choline content of the sweat was found to be 80—100 times normal and of the serum 2—15 times normal during menstruation. Intravenous injection of 0·5 g. of choline chloride in women resulted, in half the cases investigated, in a diminished rate of coagulation of the blood. G. W. R.

Relation of the Chemical Constitution of certain Organic Arsenical Compounds to their Action on the Optic Tract. A. G. Young and A. S. Loevenhart (*J. Pharm. Expt. Ther.*, 1924, **23**, 107—126).—Arsenical drugs with quinquevalent arsenic, such as atoxyl, arsacetin, and tryparsamide, frequently affect the optic tract and may produce blindness, whilst certain tervalent arsenic compounds, such as arsphenamine, do not have this effect. Sixteen arsenical compounds of similar constitution were tested by intravenous administration to rabbits, and it was found that the valency of the arsenic was not the most important factor. Optic lesions were produced by compounds containing an amino group or a substituted amino group in the para-position to the arsenic, but were not produced when the amino group was in the ortho- or meta-position. E. M. C.

Effect of Compounds Related to Hydrazine in Producing Anhydræmia and Experimental Anæmia. M. Bodansky (*J. Pharm. Expt. Ther.*, 1924, **23**, 127—132).—The destruction of red corpuscles by subcutaneous injection into dogs of certain hydrazine derivatives has been studied with a view to the experimental production of anæmia. Hydrazine gave a temporary increase in blood concentration (anhydræmia) followed by a slight anæmia. Phenylhydrazine, acetylphenylhydrazine, and *p*-bromophenylhydrazine produce rapid destruction of red corpuscles; methylphenylhydrazine and diphenylhydrazine have similar although less marked effects, whilst *s*-di*iso*propylhydrazine, hydrazobenzene, and 2 : 2′-azobispropane cause a moderate amount of destruction. Mild anæmias were produced in rabbits by azobenzene, azoxybenzene, diazobenzene, and aminoazobenzene; diphenylcarbazide and *p*-hydrazinobenzoic acid have no effect on the blood. Compounds which are especially destructive of liver-tissue were found most effective in producing anhydræmia.
E. M. C.

Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. O. SCHÖBL (*Philippine J. Sci.*, 1923, **23**, 533—542).—Chaulmoogra oil and its derivatives exert, *in vitro*, a pronounced growth-inhibiting action on *Bacillus tuberculosis*. This inhibition is specific and is noticeable at dilutions of the oil at which no inhibition of non-acid-fast bacilli can be discerned. Oils obtained from plants related to *Taraktogenos Kurzii* have a property similar to that of chaulmoogra oil with regard to *B. tuberculosis*. *Hydnocarpus Wightiana*, *H. alcalœ*, *H. subfalcata*, and *H. venenata*, all containing the optically active acids, show antiseptic power *in vitro*, decreasing in the order mentioned. Oil derived from *Gynocardia odorata*, a plant closely related to *T. Kurzii*, was inactive towards *B. tuberculosis*; it lacks the optically active fatty acids. The growth-inhibiting power of the sodium salts of chaulmoogra oil acids appears to vary, the soap made from the total fatty acids inhibiting the growth of *B. tuberculosis* to a higher degree than does that made from a fraction of the acids. A sodium salt prepared from the isolated hydnocarpic acid approaches closely in strength the soap from the total fatty acids, whilst the sodium salt of chaulmoogric acid is much weaker in its action. H. C. R.

Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. II. Comparison of the Antiseptic Power of Chaulmoogra Oil with that of other Vegetable and Animal Oils. O. SCHÖBL (*Philippine J. Sci.*, 1924, **24**, 23—27).—A series of 42 different oils, including vegetable oils, essential oils, and animal oils, was examined according to the technique previously described for their inhibitory effect on the growth of *Bacillus tuberculosis*, *Vibrio cholerœ*, and *Staphylococcus* in glycerol meat infusion agar culture. Certain vegetable oils other than those containing optically active fatty acids inhibited the growth of acid-fast bacteria *in vitro*. None of the vegetable oils proper that were investigated inhibited the growth of acid-fast bacteria at such a high dilution as do the chaulmoogra and *Hydnocarpus* oils, which contain optically active fatty acids. Certain essential oils and oils containing volatile constituents, such as cinnamon oil, show a very high selective inhibitory action on acid-fast bacteria. H. C. R.

Toxins. I. Ricin. P. KARRER, A. P. SMIRNOFF, H. EHRENSPERGER, J. VAN SLOOTEN, and M. KELLER (*Z. physiol Chem.*, 1924, **135**, 129—166).—The purified products obtained by the fractionation of ricin, tested by intravenous injection into rabbits, showed an extraordinary constancy of toxicity, the lethal dose being 0·005 to 0·003 mg. per kg. live weight. Ricin is not adsorbed by kaolin; basic aluminium sulphate adsorbs the toxic constituents, whilst aluminium hydroxide adsorbs the less toxic constituents. Fractional precipitation with salts of heavy metals affects ricin preparations adversely. The destruction by trypsin of ricin, as measured by the toxicity of the digestion mixture and of the undigested residue at different stages, ran parallel to the protein hydrolysis, so that the toxic action of ricin appears to be a function

of the protein. It has not been possible to concentrate the toxic principle beyond a certain point, and yet such preparations are not single substances, since less toxic materials may be removed by adsorption and different preparations give different equivalents on titration in alcohol. A complete analysis by the Fischer and Dakin methods has been made of the amino-acids after hydrolysis of the protein. The original must be consulted for details.

E. M. C.

Comparison of the Activities of Antiseptics on Bacteria and on Leucocytes. A. Fleming (*Proc. Roy. Soc.*, 1924, **B, 96,** 171—180).—Leucocytes have a rapid lethal action on bacteria, distinct from their phagocytic action. There is, for all common antiseptics, with the possible exception of flavine, a range of concentrations (below that at which bacteria are killed) within which the bactericidal power of leucocytes is destroyed ("antibactericidal zone"). Thus the presence in blood of an antiseptic in a concentration within this zone, so far from preventing the growth of bacteria, may actually favour it. W. O. K.

Mechanism of the Action of Bismuth Derivatives in Trypanosomiases and Spirilloses. C. Levaditi and S. Nicolau (*Ann. Inst. Pasteur*, 1924, **38**, 179—239).—A detailed account of work already published in brief (*Compt. rend.*, 1923, **176**, 1189). W. O. K.

Degradation of Starch by Animal Amylases. O. Holmbergh (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 33, 1—5).—The author has investigated the action on 2% starch solution of glycerol extracts of dry, powdered liver, prepared by treating the minced liver with ether and acetone. As these preparations contain maltase as well as amylase, parallel experiments were made in all cases with substrates containing only maltose. The velocity of the amylolytic reaction is diminished to the extent of about 32 (75)% by the presence of 0·4 (3)% of maltose. Liver-amylase is far more sensitive to the influence of maltase than is malt-amylase. When the maltose formed is removed by either dialysis or fermentation, the hydrolysis of the starch is quantitative. In all the experiments the reaction of the medium was adjusted to p_H 6·9, which is the optimum acidity for amylolytic changes.

Dialysis of 1% starch solution proceeds far more rapidly when the starch is prepared by Zulkowski's method (A., 1880, 865) than when Lintner's soluble starch is used. T. H. P.

Action of Potassium Iodide on the Saccharification of Starch by Various Amylases. O. Holmbergh (*Biochem. Z.*, 1924, **145**, 244—248).—Potassium iodide inhibits the formation of maltose from starch by the action of malt-amylase, the action in this respect resembling that on liver-amylase (cf. Holmbergh, *Z. physiol. Chem.*, 1924, **134**, 68). It increases the similar actions of salivary and pancreatic amylases. The two latter amylases therefore differ from liver-amylase. The varying extents to which dextrins and maltose are formed by the action of liver-amylase on

starch have been investigated in concentrations of potassium iodide varying from 0·1*N* to 2·0*N*. The amount of maltose formed when the achromic point is reached diminishes with increasing concentrations of the iodide, but the rate of formation of the dextrins themselves is increased. J. P.

Hydrolysis of Starch by Emulsin. R. KUHN (*Z. physiol. Chem.*, 1924, **135**, 12—15).—Preparations of emulsin from both bitter and sweet almonds brought about a considerable hydrolysis of soluble potato starch, at an optimum acidity of p_H 5·5. A specially purified sample of the enzyme converted the amylase of the starch grains quantitatively into maltose. E. M. C.

Digestion of Gums by Organisms and Enzymes. Digestion of Cherry Tree Gum *in vitro*. A. VOSKRESSENSKY (*Bull. Soc. Chim. biol.*, 1924, **6**, 226).—Experiments are recorded on the breaking down of cherry tree gum, as indicated by the production of reducing sugars, by the enzymes of various plants, micro-fungi, yeasts, and bacteria, and by enzymes contained in various animal organs. Several enzymes, of which some occur in the digestive tract of animals, can decompose the gum to some extent, but the amount of hydrolysis is much less than can be obtained with mineral acids.

Rats can live on a ration consisting largely of cherry tree gum but not on the gum alone. Various insects and molluscs refused to eat gum. C. T. G.

Invertase. V. R. WILLSTÄTTER and K. SCHNEIDER (*Z. physiol. Chem.*, 1924, **133**, 193—228).—In continuation of previous work (A., 1923, i, 69), it has been found that direct adsorption of invertase from yeast autolysates by kaolin can be brought about without preliminary adsorption by alumina, and without the considerable dilution formerly used, if the acidity of the solution is increased to the maximum limit (*e.g.* 10% acetic acid) consistent with the non-destruction of the enzyme.

Using the above improved method, several invertase preparations have been separated into easily and difficultly adsorbed fractions, and the former have been further subdivided by fractional elution. An examination of the various fractions so obtained, furnished evidence that the nitrogen content and the activity of the enzyme preparations were not proportional. Indeed, in certain cases active preparations which failed to give any protein reactions were obtained. Since in earlier work other preparations have been obtained which were free from carbohydrates, it is proved that invertase belongs neither to the proteins nor to the carbohydrates.

After a single adsorption by this method, a preparation of high activity was obtained. When the kaolin treatment was followed by adsorption by alumina, the activity was still further increased. The stability of the enzyme during adsorption varies considerably with the acidity.

The age of the autolysate and its previous purification both have a profound effect on the adsorptive value of kaolin. Whereas

with fresh autolysates preliminary precipitation with alcohol is essential for successful adsorption, this is not the case for old autolysates. O. O.

Invertase as an Amphoteric Electrolyte and as a Colloid. H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **133**, 279—297).—Using an invertase preparation of high purity (*If* = 240—242) the authors have obtained, by electrometric determination, values of $4{\cdot}3\times10^{-11}$ and $5{\cdot}5\times10^{-11}$ for K_b, and values of $0{\cdot}9\times10^{-11}$, $0{\cdot}32\times10^{-7}$, and $0{\cdot}62\times10^{-8}$ for K_a. From the values for K_b it is calculated that the molecular weight of invertase cannot exceed 3900. Viscosity measurements showed the isoelectric point to lie between p_H=4·5 and 5; this is also the p_H for maximum adsorption of the enzyme by aluminium hydroxide. The results are discussed in the light of L. Michaelis' theory concerning enzyme action, and the conclusion is drawn that the theory is inadequate. O. O.

Invertase. E. CANALS (*Bull. Soc. chim.*, 1924, [iv], **35**, 213—217).—Hydrochloric and phosphoric acids increase the hydrolysing power of dialysed yeast invertase preparations to a slightly greater extent than when undialysed preparations are used, but with sulphuric acid the reverse is the case. E. E. T.

Influence of Stereoisomeric Sugars, Non-hydrolysable Carbohydrates, and Glucosides on the Efficiency of Yeast Invertase. Specificity of Enzymes. VI. R. KUHN (*Z. physiol. Chem.*, 1924, **135**, 1—11).—The α- and β-forms of *d*-mannose and *l*-arabinose resemble those of *d*-fructose in slowing down the action of invertase on sucrose to the same extent. β-*d*-Galactose resembles β-*d*-glucose in being more active than the α-form, although both forms of *d*-galactose are much more active than the other hexoses studied. The stereoisomeric forms of lactose, maltose, cellobiose, melibiose, gentiobiose, and trehalose are without perceptible effect. The inactivity of inulin suggests that there is no combination of inulin with the invertase. Salicin, helicin, and β-methylglucoside reduce the rate of inversion, but amygdalin is without effect. The α-methylglucoside is many times as active as β-methylglucoside. These results are in agreement with the view that the activity of invertase is determined by its power of combination. E. M. C.

Fermentation Co-enzyme (Co-zymase) of Yeast. II. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **133**, 260—278).—Using small quantities of material, fermentation has been followed in the presence of co-zymase with the following results: the fall in the rate of fermentation can be overcome by the addition of fructose diphosphate; an extract of germinating malt has no influence on the rate; glycerol has no effect, whilst toluene and alcohol exert a retardation; lævulose and dextrose are identical in their action. Zymophosphate causes fermentation to start immediately, and it is suggested that yeast always contains sufficient of this substance to initiate the fermentation. In addition

to blood, milk at p_H 5 increases the activity of the co-zymase. The co-zymase present in muscle is probably identical with that present in yeast, but it does not appear to bear any relation to the anti-neuritic or growth-promoting vitamins. O. O.

Latent Fermenting Powers of Bacteria. I—III. E. C. GREY (*Proc. Roy. Soc.*, 1924, **B, 96,** 156—170).—The general course of the decomposition occurring during fermentation by *Bacillus coli* in the presence of formates is the same whether the substrate is dextrose or glycerol. In each case, about 25% and 40% of the substrate is converted into carbon dioxide and acetic acid, respectively, but the remaining 35% is mainly lactic acid when dextrose is used, and mainly ethyl alcohol when glycerol is used. In presence of formates, glycol and malonic acid are fermented by *B. coli* with the production of acetic and lactic acids, whilst citric, malic, and tartaric acids yield carbon dioxide, acetic acid, and succinic acid. The yield of succinic acid from dextrose is decreased by the presence of formates, and this is apparently due to the ability of the bacteria to ferment succinic acid under these conditions. On the basis of these and earlier results, the author outlines a simple theory of fermentation, for details of which the original must be consulted. W. O. K.

Enzymic Transformation of Aldehydes. I. Acceleration of the Cannizzaro Reaction by Yeast. K. JOSEPHSON and H. VON EULER (*Z. physiol. Chem.*, 1924, **135,** 49—60).—The authors emphasise the importance of acidity in controlling the yields of the different products of fermentation. Acetaldehyde is stable in solutions more acid than p_H 8·5. In the presence of living yeast, removal of acetaldehyde occurs even in solutions as acid as p_H 3—4. The reaction velocity is difficult to measure owing to the changes produced by the acetic acid formed, but in the early stages the acetaldehyde decomposition is only slightly less at p_H 4 than at p_H 7. A slight removal of acetaldehyde is caused by boiled yeast suspensions and is probably due to a combination with the proteins of the yeast. *iso*Valeraldehyde gives similar results to acetaldehyde, although the reaction is considerably slower. E. M. C.

Metabolism of Pyruvic Acid in Bacteria. E. AUBEL (*Bull. Soc. Chim. biol.*, 1924, **6,** 288).—A continuation of work previously published (Cambier and Aubel, *Compt. rend.*, 1922, **175,** 71). Sodium pyruvate serves as a source of carbon for bacteria. It gives rise in cultures to carbon dioxide, hydrogen, methane, lactic, glycollic, acetic, and formic acids. The energy relationships of the reactions taking place in the formation of these substances from pyruvic acid are discussed.

Working with a bacterium isolated from the Paris water supply, it was found that considerable quantities of dextrose were converted into pyruvic acid, which was then utilised; later, lactic acid made its appearance, but whether this was formed from pyruvic acid or was the product of a separate fermentation of dextrose is uncertain. C. T. G.

Mechanism of the Production of β-Hydroxybutyric Acid by Biochemical Means. LEMOIGNE (*Compt. rend.*, 1924, **178**, 1093—1095).—Continuing previous work (A., 1923, i, 881; this vol., i, 353), the author finds that a new insoluble, crystallisable product may be obtained from macerations of bacteria of the *Bacillus subtilis* group, by means of boiling alcohol. The structure of the pure *substance*, m. p. 118—119°, has not been determined, but alkaline hydrolysis gave 1 mol. of α-crotonic acid, m. p. 72°, and 2 mols. of β-hydroxybutyric acid. The proportion of the two acids was calculated from the observed optical rotation of the alkaline mixture. A. B. H.

Yeast. V. Is Bios a Single Substance? E. J. FULMER and V. E. NELSON (*Proc. Iowa Acad. Sci.*, 1922, **29**, 371; cf. A., 1921, i, 386; *J. Biol. Chem.*, 1922, **51**, 77).—Combination of the absolute alcohol extracts of lucerne with the water extract of the residue produced greater yeast growth than either extract alone. Bios is composed of at least two yeast-growth promoting materials. CHEMICAL ABSTRACTS.

Multiple Nature of Bios. E. J. FULMER, W. W. DUECKER, and V. E. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 723—726).—An aqueous extract of lucerne was fractionally precipitated with alcohol and the four resulting fractions were tested for "bios" in a medium containing ammonium chloride, dipotassium phosphate, calcium chloride and carbonate, and sucrose, which was inoculated with yeast. The results obtained showed that bios contains at least two different growth stimulants. C. J. S.

Pancreatic Enzymes. VI. Effect of Lipase on Different Substrates. R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **133**, 229—246).—The hydrolysis of methyl butyrate by lipase is accelerated by calcium oleate, but much more so by a mixture of albumin, sodium oleate, and calcium chloride at p_H 8·9. The addition of a large amount of glycerol (33%) still further accelerates the hydrolysis. Both the rate and degree of hydrolysis are directly proportional to the amount of the enzyme present.

In the hydrolysis of triacetin by lipase, the enzyme is activated by salts of bile acids and oleic acid. As in the case of tributyrin (A., 1923, ii, 704), the increase in hydrolysis due to calcium oleate is not further emphasised by the addition of albumin. In the course of the hydrolysis, the effect due to the enzyme diminishes, and this change is due to deterioration of the enzyme.

From a study of the rate of hydrolysis of various esters by various lipase preparations it is concluded that pancreatic lipase is not a mixture of enzymes, but one single enzyme which, however, shows a quantitative specificity as regards its rate of action on different substrates. O. O.

Pancreatic Enzymes. VII. Comparison of Gastric Lipase with Pancreatic Lipase. R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **133**, 247—259).—Gastric lipase and pancreatic lipase, from the pig, differ in their behaviour towards

activators such as sodium oleate and bile salts, and towards the hydrogen-ion concentration. Further, different preparations of the one enzyme from the same source show inconsistent behaviour. These divergences can, however, be traced to contamination. When gastric lipase is purified by adsorption with kaolin and elution with ammoniacal phosphate solution containing glycerol, these differences disappear, and it is concluded that there is no difference between gastric lipase and pancreatic lipase. Lipase is not present in the organs as a zymogen. O. O.

Enzyme Action. XXV. Comparative Lipase and Protease Actions of the Flexner–Jobling Rat Carcinoma and of different Rat Tissues. XXVI. Comparative Lipase and Protease Actions of different Beef Tissues. XXVII. Comparative Enzyme Actions of Tissue Mixtures and of Tumour-tissue Mixtures in Relation to the Comparative Enzyme Actions of Tumour Extracts Alone. K. G. FALK, H. M. NOYES, and K. SUGIURA (*J. Biol. Chem.*, 1924, **59**, 183—212, 213—223, 225—235).—The activities of extracts of various tissues in hydrolysing phenyl acetate, glyceryl acetate, methyl butyrate, benzyl acetate, ethyl acetate, ethyl butyrate, methyl benzoate, ethyl benzoate, *iso*butyl acetate, and protein, were measured. By expressing the results graphically, characteristic differences between the action of the extracts from different tissues are brought out. For details, the original must be consulted. W. O. K.

Protein Studies. III. Decomposition of Silk Fibroin by Fermentation. F. WESSELY (*Z. physiol. Chem.*, 1924, **135**, 117—121).—Silk fibroin was dispersed by dissolving it rapidly in cold concentrated hydrochloric acid and neutralising with sodium hydroxide, with rapid cooling. The resulting solution was stable if it contained less than 1·5% of fibroin, but was flocculated by shaking or stirring. The fibroin could be reprecipitated quantitatively by alcohol and ether. On digestion with trypsin, about one-quarter of the fibroin separated as a jelly in 24 hours; the remaining liquid gave no precipitate with 50% alcohol, and contained little nitrogen as amino-acids or as compounds not precipitated by phosphotungstic acid. Similar evidence of decomposition by pepsin was obtained. E. M. C.

Can Copper Salts Act Simultaneously as Oxydases and Peroxydases? R. DUBOIS (*Compt. rend. Soc. Biol.*, 1923, **89**, 10—11; from *Chem. Zentr.*, 1924, i, 458).—Fehling's solution can act on luciferin, producing luminescence in the same manner as luciferase. The observations of Valdiguié (*Compt. rend. Soc. Biol.*, 1923, **88**, 1091) are confirmed. G. W. R.

Effect on Phenols and their Derivatives of Oxydases of Melanotic Tumours in Chorioidea. J. MAWAS (*Compt. rend. Soc. Biol.*, 1923, **88**, 263—265, 332—333; from *Chem. Zentr.*, 1924, i, 354).—The peroxydase from melanotic tumours in chorioidea has no effect on phenol, thymol, phloroglucinol, and naphthol.

With pyrocatechol a colour change with the formation of a precipitate is observed. Pyrogallol and hydroxyquinol are oxidised. A direct relationship appears to exist between the constitution of organic compounds and their ability to be oxidised by enzymes. For example, phenols are only attacked when the hydroxy groups are in the ortho position. The formation of a black pigment is not attributed to a tyrosinase or to the oxidation of tyrosine by a peroxydase. G. W. R.

Action of Laccase. Influence of Concentration of Guaiacol and Pressure of Oxygen. P. FLEURY (*Compt. rend.*, 1924, **178**, 1027—1030).—For concentrations of guaiacol below a certain value, the reaction velocity of laccase was proportional to the concentration of guaiacol, but at concentrations above that value it tended to become constant. Diminution of laccase concentration displaced this zone of inflection in the direction of lower guaiacol concentration. Variation of the oxygen content of the air current affected the reaction velocity only when it was decreased; a similar zone of inflection was observed, which was displaced in the direction of low oxygen concentration as the amount of laccase present decreased. The rate of diffusion of the oxygen into the solution also conditioned the activity of the laccase. H. J. E.

Liver Catalase. S. HENNICHS (*Biochem. Z.*, 1924, **145**, 286—305).—Denoting the "activity" of the catalase present by: (reaction constant) ÷ (dried residue in 1000 c.c. of the reaction mixture), it is shown that liver catalase preparations may be obtained with an "activity" of 532 by adsorption with kaolin and elution with a phosphate mixture of p_H 7·6, by which means a quantitative recovery of the enzyme is achieved. Aluminium hydroxide is also used as an adsorbent (p_H 5—7) and the elution carried out at p_H 8. Two such treatments gave a preparation with an "activity" of 521. Previous preparations of liver and blood catalase by Madinaveitia (*Diss.*, Zurich, 1912) had "activities" of 66·8 and 34·9 respectively, and it is concluded that a considerable advance has been made in purifying the enzyme. The affinity constant of the system catalase–substrate is given as K_M 22. The thermostability of catalase varies with the concentration, dilute solutions being much less stable at 60° than more concentrated solutions. J. P.

Relations between the Physico-chemical State and the Functioning of Protoplasm. Photosynthesis and Respiration. C. FROMAGEOT (*Bull. Soc. Chim. biol.*, 1924, **6**, 169—180).—Pieces of the alga *Ulva lactuca* kept in sea-water containing varying amounts of glycerol showed an output of oxygen which diminished as the concentration of glycerol was increased, and ceased when the latter reached 15%. This effect was reversible when the alga was removed from the glycerol solution provided its concentration had not exceeded 10%. The alga kept in the dark under the same conditions showed an increased absorption of oxygen up to glycerol

concentrations of 5%, above which the respiration diminished but did not cease even in concentrations of 40%. Saline solutions of the composition of sea-water and of the same p_H, but with varying concentrations, affected the photosynthetical activity markedly, the latter being at an optimum when the osmotic pressure of the solution was that of sea-water. A similar effect on respiration was not observed, but in very concentrated sea-water it was slightly diminished. It is concluded that physico-chemical alterations of the protoplasm do not affect photosynthesis and respiration in the same way, and that the former process is much more susceptible to such disturbances than is the latter. J. P.

Feeding of Plants with Aldehydes. IV. T. SABALITSCHKA. **Behaviour and Detection of Formaldehyde in Plants and Plant Substances.** T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **145**, 373—378).—Fresh leaves of cress plants grown in an atmosphere containing formaldehyde (cf. this vol., i, 475) contained less than 0·5 mg. of formaldehyde per gram, whilst the same amount of leaves after drying contained 0·2 mg., and after extraction with water and alcohol 0·1 mg. The dry residue obtained from the aqueous extract of the leaves contained no formaldehyde. Formaldehyde added to fresh rhubarb or cress leaves made into a pulp with water was fixed wholly or in part. Its presence in fresh cress leaves or in the aqueous distillate from an extract of the leaves could not be demonstrated. J. P.

Water Cultures containing Benzoic Acid. Assimilation of Benzoic Acid by Culture Plants. T. BOKORNY (*Biochem. Z.*, 1924, **145**, 306—308).—Barley seedlings grown in a medium containing benzoic acid (0·016%) appeared to absorb the latter and to give increased growth. The presence of the acid in the plants could not be demonstrated, and it is concluded that it is assimilated and serves as a source of carbon. J. P.

Nitrogenous Substances in Ripening Rye Ears. A. KIESEL (*Z. physiol. Chem.*, 1924, **135**, 61—83).—The total nitrogen content of whole rye ears increased as ripening proceeded; the increase was chiefly in the protein nitrogen, with slight increases in the base and peptone nitrogen and in the amide nitrogen. The ammonia nitrogen remained constant, whilst the amino-acid nitrogen showed a pronounced minimum in one case. Asparagine was absent in each stage. The purine bases decreased markedly as the ripening proceeded. Xanthine, guanine, adenine, and hypoxanthine were separated from one sample. Histidine could be detected only in traces. Arginine was absent, but the arginine fraction contained guanidine, a base, probably agmatine, and an unidentified base. The lysine fraction from the above sample gave tetramethylenediamine, choline, aspartic acid, and phenylalanine. None of these was identified from the second fraction and only choline from the third. This is the first definite record of the isolation of aspartic acid from plants; the possibilities of its being derived from protein hydrolysis are discussed. E. M. C.

Colloidal Properties of Winter Wheat Plants in Relationship to Frost Resistance. R. NEWTON (*J. Agric. Sci.*, 1924, **14**, 178—191).—The hardiness of wheat plants was found to be related to the imbibition pressure of the leaves in the winter-hardened condition, but not in unhardened leaves. The quantity of hydrophilic colloids contained in the press juice of hardened leaves was directly proportional to hardiness. A. G. P.

Photoperiodism in Relation to Hydrogen-ion Concentration of the Cell Sap and the Carbohydrate Content of the Plant. W. W. GARNER, C. W. BACON, and H. A. ALLARD (*J. Agric. Res.*, 1924, **27**, 119—156).—The variations which occur in the habit of plants exposed to different day lengths (*ibid.*, 1920, **18**, 553) extend to the acidity of the sap, the carbohydrate content, and the water content of the tissues. Short day plants exposed to long day illumination show a progressive increase in acidity, particularly at the growing point, until the upper parts are more acid than the lower parts. Exposure to short day illumination results in a transitory period of decreased acidity followed by a moderate increase which persists until flowering is initiated. In this case, the acidity in the upper parts is not as high as that found in the lower parts of the plant. The low acidity of the embryonic flower-bud increases to a maximum in the unfolded blossom, in contrast to the developing seed in which there is a decrease in acidity during active growth. Long day plants exposed to short day periods show a low level of acidity, which increases when the day length is increased. *Helianthus annuus*, which is intermediate between the long day and the short day groups, shows changes in acidity which may be typical of either group. Transfer of Cosmos plants from a long to a short day caused a marked increase in reducing sugar in the upper portion of the stem within 48 hours of the transfer. After 2 days the increased sugar was present as polysaccharide, but 12 days later, after the flower-buds appeared, the sugar was present as monosaccharide. At the same time, a considerable increase in the water content of the tissues had occurred. O. O.

Changes in Hydrogen-ion Concentration Produced by Growing Seedlings in Acid Solutions. J. DAVIDSON and E. T. WHERRY (*J. Agric. Res.*, 1924, **27**, 207—217).—Wheat seedlings, after growing for several days in tap-water or dilute nutrient solutions, were transferred to dilute solutions of nitric, phosphoric, sulphuric, or hydrochloric acid, and the changes in p_H values observed. The greatest reduction in acidity was with nitric acid for young seedlings and with phosphoric acid for older seedlings. The importance of these acids in plant nutrition suggests that the initial changes of reaction in culture media are due to absorption rather than to neutralisation of the acids by root excreta. The reduction of acidity was less for seedlings grown in nutrient solutions lacking the corresponding anion, owing, apparently, to functional disturbances. Large reductions of acidity in solutions of organic acids were ascribed to the action of micro-organisms. E. M. C.

Insecticides. I. Isolation and Constitution of the Active Constituent of Dalmatian Insect Powder. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, **7**, 177—201).—The insect powder obtained from the flowers of *Chrysanthemum cinerariifolium* Bocc., was investigated by Fujitani (A., 1909, ii, 825), who obtained from it a highly insecticidal, viscous oil which he termed pyrethrone. By alkaline hydrolysis of this he obtained an alcohol, pyrethrol, and an acid, both of which were inactive. Fujitani's viscous oil is found to contain about 50% of inactive substances, from which the pyrethrol is derived. There are two active constituents present in the oil, termed *pyrethrine* I and II, esters of a ketonic alcohol, *pyrethrolone*, combined with *chrysanthemumcarboxylic acid* and *chrysanthemumdicarboxylic acid*, respectively. The crude oil, the yield of which is 0·5% of the weight of the powder, forms a crystalline mixed semicarbazone, from which the *semicarbazone* of pyrethrine I can be obtained almost pure, m. p. 122—123°. By hydrolysis of the mixed semicarbazones, with methyl-alcoholic sodium hydroxide, the *semicarbazone* of pyrethrolone is obtained, m. p. 200° (decomp.), and by acid hydrolysis of this, the alcohol itself, *pyrethrolone*, a colourless, optically active liquid, b. p. 110—112°/0·1 mm. The acid of pyrethrine I, *chrysanthemumcarboxylic acid*, is an optically active liquid, b. p. 135°/12 mm., and that of pyrethrine II, *chrysanthemumdicarboxylic acid*, is a more viscous, optically active liquid, b. p. 120°/0·1 mm. Neither the alcohol nor the acids have insecticidal properties. The insect powder contains the two active substances, I and II, in the proportions of about 2 : 3; the former is the more active, killing moths at a dilution of 1 in 10,000 in 10 to 20 minutes, whilst the latter takes twice as long (cf. this vol., i, 510, 521, 522, 523). E. H. R.

Phlobaphens. M. DITTMAR (*J. Amer. Pharm. Assoc.*, 1923, **12**, 680—688).—Phlobaphens can be salted out from solution, but if the salt be removed by osmosis the phlobaphen again enters into solution. The dark red solution of a phlobaphen in ethyl alcohol may be reduced by boiling with zinc dust, but the product gradually becomes coloured by atmospheric oxidation. The phlobaphens, which vary considerably in composition, yield oxalic acid when boiled with nitric acid, but when boiled with dilute sulphuric acid do not yield dextrose, although some colour changes result.

CHEMICAL ABSTRACTS.

Essence of the Carnation. M. L. S. GLICHITCH (*Bull. Soc. chim.*, 1924, [iv], **35**, 205—207).—The essence extracted from the flowers (0·003% yield) by distillation in steam was a pale green solid of greasy taste and touch with an intense odour resembling that of certain aliphatic aldehydes; m. p. 35—37°; d_{40}^{40} 0·869; $[\alpha]_D^{29\cdot 5}$ −8·28° (c=3·148 in benzene). From it a branched chain heptacosane, m. p. 53—55°, was isolated in 31% yield. Other paraffins were also present. Inconclusive evidence of an acetylated compound and of a substance of aldehydic or ketonic nature was obtained. E. E. T.